CHAPTER- 2

LITERATURE REVIEW

Glasses, the non-crystalline amorphous solid are formed from extremely viscous liquids. These materials are found to possess ionic as well as covalent bonding interaction. The American Society for Testing and Materials (ASTM) [Yamane et al 2000] defined glass as an “inorganic product of fusion” which has been cooled to a rigid condition without crystallization. The concern was mostly, on which of the chemical compositions has a greater glass forming tendency and the factors that play a significant role in ascertaining the ease of glass formation. This chapter presents a review of the literature beginning with the theoretical aspects of glass transition, formation, preparation, characterization and applications by various research groups.

2.1 Structural models for Glass Transition

The term ‘glass’ was a debate among most of the scientists and they regarded this as covering all non-crystalline solids, that show a glass transition regardless of their preparation method. The glass transformation temperature ‘\(T_g\)’ refers to the temperature at which the glass transforms from a higher temperature glassy state to a super-cooled liquid state. Rao [1979] found that glasses which possess low fictive temperature relaxes slowly and glasses which possesses high fictive temperature relaxes more rapidly. The specific volume ~ temperature graph of a glass forming liquid is shown in Fig. 2.1. When the melt of the glass is cooled quickly from melting temperature (\(T_m\)), there will be a rapid increase in viscosity and it gets supercooled to a very low temperature with corresponding change in volume or entropy. The melt reaches the glassy state at a characteristic temperature known as glass transition temperature (\(T_g\)). This transition will be accompanied by abrupt change in the second
order thermodynamic quantities like specific heat \( (C_p) \), thermal expansivity \( (\alpha) \) and compressibility \( (\beta) \) near the transition temperature \( (T_g) \).

**Fig. 2.1. Variation of specific volume as a function of temperature.**

Fig. 2.2 shows the specific volume changes during the cooling of a melt. While cooling along the line ‘AB’, there is a volume contraction of the melt, and if the cooling rate is sufficiently slow, this is followed by a fast, discontinuous change (BH) in volume at the melting point \( (T_m) \) and the specific volume of the crystal slowly decreases with decrease in temperature (HG). Rapid cooling of the liquid can suppress crystallization producing a supercooled liquid (BC). In the vicinity of glass transition ‘\( T_g \)’ gradual solidification or the formation of glass takes place. At the glass transition temperature, the thermal energy becomes insufficient for any further configurational adjustments to take place within a reasonable amount of time. However, the glass transition depends on the rate of cooling. For faster cooling rate, the glass transition is higher \( (T_{gf}) \) and for a slower cooling rate, the glass transition is lower \( (T_{gs}) \). Below the transition temperature, the specific volume of the glass slowly decreases with decreasing temperature, similar to that of the crystal. In the Fig.2.2, ‘CE’ represents the change in
specific volume of fast cooled glass and ‘DF’ represents the change in specific volume of slow cooled glass.

Fig. 2.2. Specific volume changes with temperature during glass transition.

Entropy too follows a similar pattern of change. If an infinitely slow cooling rate is employed, in which the entropy of the supercooled melt continue decreasing till it reaches the point ‘I’, it is found that the entropy of the disordered supercooled liquid will become equal to the entropy of the ordered crystalline solid at ‘I’, which is not permissible under the laws of thermodynamics. This thermodynamic catastrophe is termed as Kauzmann paradox [Kauzmann 1948], which is avoided by the occurrence of glass transition so that the entropy of the supercooled liquid never reaches the point ‘I’. Glass transition thus appears to be an unavoidable thermodynamic consequence when a liquid is supercooled to sufficiently low temperature. Thus glass transition is a measure of the approximate temperature where the supercooled liquid on cooling converts to a solid or where the solid on heating behaves as a viscoelastic solid. $T_g$ is generally defined as the temperature at which the highest rate of change of viscosity with temperature occurs in the process of solidification from the supercooled liquid.
The viscosity changes during cooling of a liquid is as shown in Fig. 2.3 [Raghavan V 1993]. If the crystallization takes place on slow cooling, the viscosity abruptly increases (MP) at the freezing temperature ($T_m$) to about $10^{20}$ Pas and on further cooling, the viscosity steadily increases (PQ) to about $10^{30}$ Pas. When the rate of cooling is rapid, it gives rise to supercooled liquid (MN) and the variation of viscosity with decrease in temperature is shown through the curve ‘LMNO’ in the Fig. 2.3. The viscosity gradually increases with decrease in temperature and attains high value at low temperature. Thus the highest rate of change of viscosity with temperature occurs around $10^{12}$ Pas at the glass transition temperature ($T_g$) and provides a point of distinction between a glass and a supercooled liquid.

![Fig. 2.3. Viscosity changes during cooling of a liquid.](image)

Viscosity and other transport properties usually vary exponentially in the supercooled regions and the viscosity variations in the supercooled region often exhibit a non-Arrhenius behavior in many glass forming melts [Angell and Moynihan 1969].
Angell and Moynihan have classified glass forming liquids as ‘strong’ or ‘fragile’. The viscosity and relaxation times of strong liquids are found to obey Arrhenius behavior, whereas the same quantities are found to exhibit marked deviations from Arrhenius behaviour in fragile liquids. Silica (SiO$_2$) and O-terphenyl are prototypical strong and fragile liquids respectively. Strong liquids, such as SiO$_2$ and germanium oxide (GeO$_2$) have tetrahedrally coordinated network structures, whereas the molecules of fragile liquids exert largely non-directional, dispersive forces on each other which is evident from Fig. 2.4.

Fig. 2.4. $T_g$ scaled Arrhenius representation of liquid viscosities showing Angell’s strong-fragile pattern [Angell et al 2000].

In order to understand the various features of glass transition, many modelistic approaches have been made in the literature [Parthasarathy et al 1983]. All such theoretical approaches attempt to describe the thermal variation of liquid property such
as volume, entropy or enthalpy and seeks to correlate the glass transition as a thermal event in the behaviour of supercooled liquid. Ernst Ising [1925] proposed a simple mathematical model of phase transition which explained the abrupt changes of states that occurs when water freezes or a cooling lump of iron becomes magnetic. Free volume model is based on the concomitant decrease in volume and fluidity of glass forming region in the supercooled region [Cohen 1959 and Turnbull 1961, 1970]. Therefore glass transition has been related to the decrease of free volume associated with particles. Below a critical value of free volume, particle transport is considered impossible. Molecular transport therefore ceases resulting in a frozen phase known as glass. This model failed to account for the pressure dependence of \( T_g \). It was also not applicable to well-known covalently bonded inorganic glass forming liquids such as \( \text{SiO}_2, \text{B}_2\text{O}_3 \) and \( \text{P}_2\text{O}_5 \).

The configurational entropy which was developed by Gibbs and co-workers [Gibbs and DiMarzio 1958; Adam and Gibbs 1965] related entropy with the help of thermodynamical theory of glass transition. In another approach to the glass transition, Goldstein [1969, 1976a, 1977] put forth that, the configurational entropy of a liquid is thought to arise from a number of configurations available to the system because of local re-arrangement of the constituent particles. During the quenching of the melt, the configurational entropy decreases. This requires participation of more and more particles to rearrange the local structure, which leads transport event to occur [Adam et al 1965]. At sufficiently low temperature, the configurational entropy may go to zero and in such cases a second order transition must occur. But in real situations, there is an intervention of the kinetics of solidification, due to long relaxation times and thus the glass transition occurs even before the configurational entropy becomes zero. The bond-lattice model [Angell et al 1972] describes the glass structure as an amorphous
network of bonds of any type including secondary bonds and random thermal excitation which leads to heat capacity changes around \( T_g \). When a glass is heated, these bonds are said to be broken due to thermal excitation. This leads to a change in volume (\( \Delta V \)) and entropy (\( \Delta S \)) and the corresponding change in heat capacity is given by

\[
\Delta C_p = \frac{\Delta H^2}{RT^2f(1-f)}
\]  

where ‘\( \Delta H \)’ is change in enthalpy and ‘\( f \)’ is the fraction of the bonds broken during the excitation. The variation of \( \Delta C_p \) with the temperature does not exhibit any singularity but shows an asymmetrical peak like behaviour. The peak temperature identified as ‘\( T_g \)’ in this approach is determined by \( \Delta H \). However, this model could predict a rapid rise in \( C_p \) near \( T_g \) and no discontinuity has been observed as in real glass transitions. This model extends the concept of Ising model of phase transition in the crystalline state to the glass transition in glasses with moderate success.

Rao K J [1984] was the first to put forth the cluster model of glass transition. According to this model, the glass consists of ordered regions of ‘clusters’ embedded in connective tissue material of lower density. The supercooled liquid is characterized by fairly large-scale fluctuations in density and composition, which nucleates into ordered clusters at low temperatures. However, the size of the clusters does not exceed a self-limiting value of 50 -100 Å. When the temperature is lowered to glass transition temperature, major part of the melt is transformed into clusters and these clusters impinge on each other and transform into a solid. The remaining part simply freezes as tissue between the clusters. Here, the relative size of the clusters is used as the order parameter.
This model suggests a direct relation between the vibrational frequency ($\nu$) of the cation in an ionic glass and its glass transition temperature ($T_g$) [Angell et al 2000]. Since the vibrational frequency can be expressed as

$$\nu = \left( \frac{1}{2\pi} \right) \sqrt{\frac{f}{\mu}}$$

(2.2)

where ‘$f$’ is the force constant and ‘$\mu$’ is the reduced mass, the relation between $\nu$ and $T_g$ can be examined independently by varying $\mu$ and $f$. The effect of varying $\mu$ and $T_g$ while holding force constant, has been investigated [Exarhos 1972] and the results are found to be consistent with the cluster model.

In computer simulation model, computer simulation provides valuable insight with regard to the effect of several types of pair potentials on the phenomenon of glass transition. Computer simulation methods [Frenkel and McTague 1980] such as molecular dynamics or Monte Carlo method have been used to study glass transition in simple liquids. The existence of glass transition has been noted from the variation of density, enthalpy or pair distribution function when temperature or pressure is altered. In these studies, the glass transformation range is broader and occurs at a higher temperature than the corresponding experimentally observed transitions because of the short time scales in computer simulations.

In spite of the ambiguities in arriving at a general model to explain all the features of glass transition, this parameter has been extensively used to understand glass structure. $T_g$ has been related to various properties like variation in cohesive energy [Rao B G et al 1984], liquidus temperature [Narasimhan et al 1978], formation of non-bridging oxygens [Moustafa et al 1998; Mekki et al 2003; Al-Hajry et al 2006] etc.
2.2 Theories of Glass formation

The earliest theory of glass formation was based on the study by Goldschmidt [Goldschmidt et al 1926] that glasses of the general formula $R_nO_m$ form most easily, when the ratio of ionic radius of the cation ‘$R’ to the radius of oxygen ions ‘$O’ lie in the range 0.2 to 0.4. He was of the opinion that only melts containing tetrahedrally coordinated atoms form glasses during cooling. This theory was empirical and could not explain why only tetrahedral coordination should be favourable. A few years later, Zachariasen [1932] extended the idea of Goldschmidt and attempted to explain why coordination numbers might favour glass formation. Because of the explanation of the same, this model was widely used for glass formation and this paper has been widely cited. Zachariasen concluded that the mechanical properties and density of an oxide glass are similar to those of the corresponding crystal. He further pointed out that because of the random network, internal energy of glass is only 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.

Zachariasen considered the relative glass-forming tendency of oxides and concluded that the basic condition for glass formation is that a substance can form an extended three-dimensional network which lacks periodicity but with energy content comparable with that of the corresponding crystalline network. From this condition he brought out four rules for oxide structure that allow selection of those oxides that tend to form glasses. The Zachariasen rules are: (i) oxygen atoms are linked (bonded) to more than two atoms (ii) oxygen coordination around glass forming cations is small, 3
or 4 (iii) cation polyhedra share corners and not edges or faces (iv) at least three corners are shared.

The continuous Random Network model first put forward by Zacharaiesen, envisages a glass forming material to possess a covalent network. This model has basic structural units similar to those in crystalline solids. These units are linked together by an irregular three-dimensional network. In fused silica, the basic structural unit is \([\text{SiO}_4^{2-}]\) (tetrahedron), where randomness is achieved by varying the relative orientations of adjacent tetrahedrals throughout the structure, by allowing the Si-O-Si angle to take a range of values. The Si-O-Si angle ranges from about \(120^0\) to \(180^0\) with a mean value of about \(144^0\). On the other hand, the O-Si-O angle does not differ appreciably from the ideal tetrahedral angle. The Zacharaiesen model has been supported by XRD studies of SiO\(_2\) [Mozzi and Warren 1969]. Since glass is usually obtained by supercooling a melt, any material therefore in principle should form a glass by sufficient fast quenching [Turnbull 1969]. However, very few glasses of simple components like SiO\(_2\), B\(_2\)O\(_3\), SeO\(_2\), GeO\(_2\), ZnCl\(_2\), P\(_2\)O\(_5\), As\(_2\)S\(_3\), etc exist.

Sun [1959] too proposed a model based on bond strength between oxygen and other atoms in the glass former and suggested that the bond strength should be above 80 kcal mole\(^{-1}\). But, it was found that such high bond strengths make viscous flow very difficult. Tammann [1932] tried to show that glass formation occurs when the stages of nucleation and growth are well separated in temperature. Rawson [1967] modified the model suggested by Sun by relating glass forming tendency to the ratio of bond-strength to melting temperature. Uhlmann [1972] estimated the critical cooling rate for glass formation from Temperature-Time-Transformation (TTT) diagram. When the melt is cooled very quickly, it is possible to reduce the mobility of the molecules to a point
where they cannot move around to order themselves periodically. This concept can be expressed on TTT (Time temperature transformation) graph (Fig. 2.5).

**Fig. 2.5.** T-T-T diagram for glass forming melt.

Each TTT diagram has an extremum, which reflects the competition between the driving force for crystallization and mobility of molecules, atoms or ions and represents the least time required for a given fraction to get crystallized. Formation of glasses occurs only at cooling rates above the critical cooling rates and this has been verified for a number of glass systems. A qualitative approach relating to glass formation to the rate of cooling rate of nucleation and crystal liquid interface viscosity was given by Turnbull [1974]. He pointed out that melts have to be cooled very rapidly through a temperature region in order to prevent crystallization and to ensure glass formation. Under proper experimental conditions, any material can be formed as a glass. Kinetic theory outlines nucleation and crystal growth rate allows the prognosis of these conditions. Analysis of the results of the kinetic studies leads to the information about the ease of formation of glasses from melts. In particular, the dependence of viscosity on temperature is a significant factor in ascertaining the glass forming ability of a glass melt. The earlier theories of glass formation which were based on structural and
bonding considerations correlate quite well with the observed trends. Among the various methods, the use of TTT curves and views of critical cooling rate provide direct experimental methods for comparison for glass forming ability.

The term ‘network glass former’ is adopted for the oxides capable of forming the glass network. As$_2$O$_3$, P$_2$O$_5$, V$_2$O$_5$, GeO$_2$, SiO$_2$, B$_2$O$_3$, etc are some of them which have been reported in literature [Minami et al 1980; Magistris et al 1981; Elliott et al 1986; Spence et al 1989; West et al 1989; Paul 1990]. A lot of work on the structural and physical properties of different oxide glasses having TeO$_2$ and P$_2$O$_5$ as glass former has been reported [Minami et al 1980; Pal et al 2001; Mogu’s Milankovi 2003; El-Desoky et al 2007]. Glasses of alkali composition have been extensively studied over the years to elucidate the nature and relative concentration of various units constituting the glass network [Chandra 1981]. Veeranna Gowda et al [2004] proposed oxides such as silicates, borates, phosphates, germinates, aresenates etc as glass formers and vanadates, molybdates, tungstates etc as ‘conditional glass formers’ which form glasses in conjunction with other glass formers. The structure of oxide glasses can be well characterized by the presence of extensive two and three-dimensional networks which are modified by the addition of alkali or alkaline earth oxides.

Thus it appears that the structural, thermodynamic and kinetic theories for glass formation have been developed somewhat independently of each other and in order to understand some generalised criteria for glass formation, all these factors have to be collectively taken into account.

2.3 Microwave processing

Microwaves (frequencies of 0.3 GHz to 300 GHz and wavelengths of 1m to 1mm) lie between radiowave frequencies (RF) and infrared (IR) frequencies in the
electromagnetic (EM) spectrum. Microwaves can be reflected, transmitted or absorbed. The absorbed microwave energy is converted into heat within the material, resulting in an increase in temperature. Gases, liquids and solids can interact with microwaves and get heated.

Reviews by Clark and Sutton [1996] and Sutton [1989, 1992] gave a broader picture of status on microwave processing. Lewis [1992] reported about microwave processing readily adopted by polymer technologists especially in the field of the vulcanization of rubber. Researchers in Ukraine and Russia used high frequencies (37 and 84 GHz) for rapid coating of plastics in oil pipes, in glazing of ceramics, soldering and brazing treatment of polymers, composites and in the synthesis of semiconductors and other materials [Paton et al 1993]. Das et al [2009] reported an overview of the microwave processing of a variety of conventional as well as advanced materials. Selective heating of materials (Thostenson and Chou 1999) and unique microstructures and improved product yield are some of the advantages of using microwaves [Sutton 1989].

Osepchuk [1984] was the first one to report about the wide use of microwave ovens which can work at a frequency around 2.45 GHz. These frequencies are commonly used for microwave heating because of two reasons. The first is that they fall in one of the industrial, scientific and medical (ISM) radio bands and the second reason is that the penetration depth of the microwaves is found to be greater for these low frequencies. The essential features of a typical multimode domestic microwave oven is illustrated in Fig.2.6 and that of a magnetron in which the microwaves are generated [Collin 1966] is shown in Fig. 2.7.
Fig. 2.6. Essential features of a microwave oven.

Fig. 2.7. Features of a magnetron in a microwave.
Sutton [1989] suggested the application of microwave energy for the synthesis of various materials such as metals, ceramics and composites and informed about the several advantages that it possess over conventional heating techniques. It mainly possess improved product yield, unique microstructure and properties, energy savings, reduction in manufacturing cost and synthesis of new materials.

Das et al [2009] presented an overview of the microwave processing of different materials and described some applications of microwave heating to materials processing. Finally, Oxana et al [2010] revealed the use of microwave (MW) radiation in glass processing and compared it to the usual processing techniques, such as glass melting, sintering, sealing, devitrification, coating, reinforcement with various substances, deposition by layers etc.

Rao K J et al [1995] revealed the popular ideas of interaction of microwaves with matter and have suggested preparation of several materials through different types of reactions assisted by the use of microwaves. He showed that microwave heating is as a result of energy transfer from the electromagnetic field to the material. Response of a material when exposed to an electromagnetic field of frequency ‘f’, is determined by its complex dielectric constant

$$\varepsilon^* = \varepsilon' - i\varepsilon''$$

(2.3)

where $\varepsilon'$ is the real part of permittivity which gives a measure of charge storing capability of the material. Bound charges which oscillate in-phase with the applied field (resulting in current which is 90$^\circ$ out of phase with voltage) contributes to $\varepsilon' \cdot \varepsilon''$ Is the imaginary part of permittivity, which is a measure of energy loss or energy dissipative nature of the material.
The imaginary part of the permittivity is given by,

\[ \varepsilon'' = \frac{\sigma}{2\pi f \varepsilon_0} \]  

(2.4)

where \( \varepsilon_0 = 8.85 \times 10^{-12} \text{ F/m} \), \( \sigma \) is the effective conductivity of the material in S/m.

Both bound and free charges in the material oscillate 90\(^\circ\) out of phase with the applied field (resulting in current which is (90 - \( \delta \)) out of phase with voltage) as shown in Fig.2.8. \( \delta \) is called dissipation factor or loss angle which determines the energy loss due to dissipation in the dielectric and is responsible for the volumetric heating of the material.

![Fig. 2.8. Dielectric loss mechanism](image)

The primary sources of dissipation in a material are the responses of space charges, ionic motions, dipolar reorientations and electrons in variety of bonding conditions. As frequency of applied field increases, these sources of dissipation become ineffective because the species responsible for a particular mechanism cannot follow the change in direction of the field. All the above mentioned loss mechanisms are collectively expressed by a loss factor.

\[ \tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\sigma}{2\pi f \varepsilon' \varepsilon_0} \]  

(2.5)
Microwave heating in a lossy material is the result of absorption of microwave energy by the material as microwaves pass through it. If the electric field is considered to be uniform throughout the volume of the material, then the microwave power absorbed per unit volume is given by,

\[ P = \sigma |E_i|^2 = 2\pi f\varepsilon_0 \varepsilon' \tan \delta |E_i|^2 \]  \hspace{1cm} (2.6)

where ‘\(E_i\)’ is the magnitude of internal electric field.

It can be noted from equation (2.6), that the power absorbed varies linearly with relative permittivity, frequency of the applied field, square of the internal electric field and \(\tan \delta\). Internal electric field in a material depends on the size, geometry and location of the material within the microwave cavity. Also it is evident from equation (2.6) that ‘\(\tan \delta\)’ and ‘\(\varepsilon'\)’ are material properties and ‘\(f\)’ and ‘\(E_i\)’ instrument variables. Therefore, it is possible to control the power absorbed by a material by changing the frequency and microwave power.

The distance from the surface at which the incident power is reduced to one-half is defined as the penetration depth,

\[ D = \frac{\lambda_0}{8.868 \pi \tan \delta \left( \frac{\varepsilon'}{\varepsilon_0} \right)^{\frac{1}{2}}} \]  \hspace{1cm} (2.7)

where ‘\(\lambda_0\)’ is the incident wavelength. ‘P’ and ‘D’ gives an idea about suitability of a material for microwave heating. Knowledge of penetration depth and the power absorbed per unit volume are very important while processing thick materials. ‘D’ is higher for higher wavelength or lower frequency. But according to equation (2.5), low frequencies result in lower induced electric field in the material, which in turn causes less heating. Thus an optimum range of microwave frequency should be used for
material processing and the commonly used microwave frequencies are 0.915 GHz and 2.45 GHz. The loss factor of the material denoted by \( \tan \delta \) is found to be temperature dependent. This may lead to an exponential increase in temperature (runaway) and the phenomenon is known as thermal runaway, which causes undesirable hot spot in the material. This can be avoided by controlling the power [Kenkre et al 1991]. Thus the heating takes place because of the interaction of microwaves with materials. Baykal et al [2001] used microwave for synthesis of boron-phosphate and found that microwave synthesis have benefits over the conventional methods such as shorter reaction time, lower energy requirements and pure phase composition.

2.4 Characterization techniques

Characterization of glasses is an important aspect in the structural study of glasses which lack long range order. It helps one to understand the behaviour of glasses under different physical parameters. The knowledge of the structural aspects, transport and optical properties are necessary for pointing out the possible applications of glasses. Physical, thermal and spectroscopic studies are the main experimental techniques generally employed to characterize the glasses. Some of the techniques employed are as follows:

2.4.1 Structural Characterization

Various types of experimental techniques have to be used to identify the structure of glasses since no single technique is capable of providing a complete characterization of a glassy matrix. In the present work X-ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), Fourier Transform Infrared (FTIR), Raman spectra, Nuclear Magnetic Resonance (NMR) and Electron Spin resonance (ESR) spectroscopies are used for the characterization of glass systems. Kuppinger and
Shelby [1985] formulated a structural model which identifies different structural units likely to be present in borate glasses. Prabhakar et al [1990] proposed a structural model where modification seems to be resulting in the formation of tetraborate and diborate units.

2.41 (a) Diffraction technique

To obtain information on the short range order and structure of glasses, X-ray diffraction studies have been used since 1930 starting with the work of Warren et al [1934]. Elliot et al [1986], Galeener [1990], Lefterova et al [2004] and many others have reported the use of X-ray diffraction to identify whether the synthesized samples were crystalline or amorphous. It helps one to study the radial distribution function from which interatomic distances and bond angle distributions. XRD is also used to extract information regarding the local structures in glasses including the nearest neighbour distances and coordination numbers. The scattering of X-ray gives a diffused pattern in glasses due to the presence of long range periodicity in glasses instead of sharp lines as in case of crystalline substances due to the absence of long range periodicity in glasses. The scattered intensity spectra, which show a few and generally broad peaks corresponding to the varying interatomic separations are used to calculate the radial distribution functions.

2.4.1 (b) Thermal characterization

The modulated Differential Scanning Calorimetry (MDSC) is widely used to study the kinetics of glass transition temperature (T_g) of the materials [Wesley et al 1964]. It has been used as a thermal analysis technique that looks at how a material’s heat capacity (C_p) changes with temperature. Mandal et al [1995] studied the T_g for binary iron-vanadate glasses and observed an increase in T_g with the increase in iron-
oxide content and explained this as due to higher cross-linking density. $T_g$ and crystallization temperatures ($T_c$) values of the iron-vanadate glasses are found to be higher than that of vitreous $V_2O_5$. Previous studies have reported that $T_g$ is strictly related to the density of cross-linking, tightness of the packing in the network, coordination of network formula etc. Ray 1974; Shelby 1975 and Mandal et al 2000 during the study of iron-vanadate glasses have found that higher vanadium concentration glasses are found to have higher electronic conductivity and the conduction was mainly due to the hopping of charge carriers between the two vanadium states and the linkages were confirmed with Differential Thermal analysis. Thermal conductivity studies were carried out on sodium alumino-phosphate glasses and the glass transition properties were related to the linkages present in the glassy network as well as with the relative proportion of $Al(PO)_6$ and $Al(PO)_4$ units [Shah et al 2003]. Karthikeyan et al [2003] correlated the results of glass transition and FTIR studies of sodium – zinc borate glasses doped with Neodymium. The $T_g$ values were correlated with the tightening of the structure with the formation of $BO_4$ and $ZnO_4$ units. Mazurin [2007] reported that the values of $T_g$ depends both on heating rates and cooling rates of glasses.

2.4.1 (c) Elastic properties

Study of elastic properties of solids are significant as their measurement gives information about the forces that are acting between the constituent atoms of solid. This helps in not only interpreting and understanding the nature of bonding in solid state but also for describing the glass structure as a function of composition [Schreiber et al 1973]. Some models were used to analyze the structure and correlate the elastic moduli of the oxide glass [Bridge et al 1983, Hizary and Bridge 1985, El Mallawamy 1980] had brought about models which helps in analyzing the structure of the oxide glass in
terms of number of network bond per unit volume, average stretching force constant, packing density and mean cross link density. Makishima and Mackenzie (1973, 1975) have worked out a theoretical model to calculate the elastic moduli of oxide glasses in terms of packing density and dissociation energy of oxide constituent per unit volume which are as follows:

\[
\begin{align*}
\text{Young’s modulus, } E_T &= 83.6 V_t \sum G_i X_i \\
\text{Bulk modulus, } K_T &= 100 V_t^2 \sum G_i X_i \\
\text{Shear modulus, } S_T &= \left[ \frac{300 V_t^2}{10.2 V_t - 1} \right] \sum G_i X_i \\
\text{Lateral stress, } L_T &= K_T + \frac{4}{3} S_T \\
\text{Poisson’s ratio, } \sigma &= 0.5 - \frac{1}{7.2 V_t} \\
\text{Fractional bond connectivity, } f_D &= \frac{4 S_T}{K_T}
\end{align*}
\]

(2.8)

The packing density ‘\( V_i \)’ of the oxide glasses of the form \( A_mO_n \) were calculated using packing factor ‘\( V_{i} \)’ of the \( i \)th component of the glass using the formula [Wei et al, 2001]

\[
V_i = 6.023 \times 10^{23} \frac{4\pi}{3} \left( mR_A^3 + nR_0^3 \right),
\]

(2.9)

where \( R_A \) and \( R_0 \) are the respective Pauling’s ionic radius of metal and oxygen. Therefore the packing density of the multi-component glass is given by

\[
V_t = \frac{\rho}{M} \sum V_i X_i
\]

(2.10)

where \( M \) is the effective molecular weight, \( \rho \) is the density of the glasses and \( X_i \) is the mole fraction of the component ‘\( i \)’. The dissociation energy per unit volume ‘\( G_i \)’
and the packing factor ‘\(V_t\)’ of each component present in the glass system can also be found from Makishima et al [1973, 1975, 1978] and Samsonav [1973]. The binding energy \(U_m\) is calculated using the formula

\[
U_m = V_t \sum G_i X_i
\]  

(2.11)

These formulae helps in correlating with the experimental results. In another approach Yamane and Sakaino [1974] expressed the Young’s modulus in terms of melting temperature of constituent oxides which is taken as a measure of cohesive forces in the network. Wei et al [2001] have tried to study the structural and elastic properties of phosphate glasses using Makishima and Mackenzie theoretical model which showed consistent results with the experimental data. Xuelu Zou et al [2001] could also estimate the values of Packing density and Elastic modulus on the basis of theoretical equations of Makishima and Mackenzie. Lowenstein [1961] found that the Young’s modulus of glasses is governed by the forces in the network and increases by placing cation of high field strength in the vicinity of the network. Thus the study of elastic properties play a supportive role in understanding the structure of glasses since the elastic constants are related to interatomic forces, nature of bonding and vibrational frequencies. Yasser Saddeek et al [2009] presented a bond compression model for the theory based analysis of the connection between the evaluated bulk modulus and the structure of a series of multicomponent sodium diborate based glasses. The main parameters in the analysis were the average stretching force constant, average atomic ring size and computed elastic moduli. The structural and physical properties of Iron doped boro-vanadate glass system prepared by normal melt-quench technique have been investigated by Virender Kundu et al [2008]. Venkata Subba Reddy et al [2009] studied the elastic properties of sodium boro - vanadate glasses using ultrasonic
velocity measurements and the variations of elastic moduli have been explained on the basis of the structural groups present in the boro-vanadate network.

2.4.1 (d) Vickers hardness

The mechanical properties of the materials can be determined by various types of hardness tests. Hardness can be defined as the resistance of the material to permanent deformation. The hardness data and size of the crack arising around the indentation pattern can be used for the determination of fracture toughness in the case of brittle materials [Dietz M 1990]. In the Vickers hardness test, a strong indenter (Vickers pyramid) is pressed into the surface of the sample with constant normal force [Gubicza 1995]. This test has been of much interest owing to the mechanical properties [Liu et al 1989; Veprek 1999; Gee et al 2003; Šimůnek 2006; Li et al 2008]. It finds application in the development of scratch-resistant glasses and covers for personal electronic devices.

2.5 Transport properties

2.5 (a) Ionic conducting glasses

Israd [1969] observed that the ionic conductivity has been of keen interest due to the absence of long range order in glasses unlike its crystalline counter parts. A rather recent and fascinating area of research has been the study of ionic conducting in glasses [Angell 1983; 1986; 1990 and 1992; Ingram 1987], as these glasses are found to have practical applications like memory devices, electrolytes in chemical sensors, capacitors, fuel cells etc. Ionic conduction in solids have been associated with jumping of an ion from one equilibrium position to an energetically similar position in the network. Early microscopic description of ionic transport in traditional oxide glasses has been to associate the cation to an equilibrium position in the intermediate
neighborhood of a non-bridging oxygen. Charles [1961] considered that a non-bridging oxygen is associated with more than one equilibrium position in its neighborhood among which the cation can execute jumps and such local motions give rise to polarization currents and manifest in ac response. There are several models proposed such as weak electrolyte model [Ravaine D et al 1977] to models based on solid state views such as the jump diffusion model [Funke 1993], the strong electrolyte model [Anderson-Stuart model 1954] and the dynamic structure model [Bunde et al 1994]. Most of these models are linked with the microscopic structure in general and the distribution of mobile cations in particular. Anderson & Stuart have provided a significant analysis of the conduction in an ion-conducting glass and their model was found to be successful in calculating the activation energy for cationic transport in alkali silicate glasses. Lowering of activation energy and increase in ionic conductivity is observed due to the addition of metal oxide to a network glass former. The fast ion conducting glasses are usually presented by the formula \( x \text{M}_2\text{O} - y \text{MnX} - A_x\text{O}_y \), where \( A_x\text{O}_y \) is a glass former and \( \text{MnX} \) is a modifier [Kamitsos et al 1986]. Glasses with a low concentration of Transition metal ion (TMI) and a high concentration of alkali or silver oxide are well known as super ionic conductors [Minami 1980, 1983; Chowdari et al 1988, 1991; Selvaraj 1985]. Ionic conduction in a glass is a thermally activated process of mobile ions that can surpass a potential barrier \( E_a \) and experimentally it has been found that in a variety of glasses, a semilog plot of the dc conductivity \( \sigma \) against temperature \((1/T)\) is quite linear and is given by the equation

\[
\sigma = \sigma_0 e^{-E_a/kT},
\]

where ‘\( \sigma_0 \)’ is the pre-exponential constant and ‘\( E_a \)’ is the activation energy. Glasses containing \( \text{Li}^+ \), \( \text{Ag}^+ \), \( \text{Cu}^+ \) salts etc exhibit high conductivity.
2.5 (b) Electronic conducting glasses

Glasses formed between metal oxides like V$_2$O$_5$, WO$_3$, MoO$_3$, Fe$_2$O$_3$, CuO, etc and P$_2$O$_5$, B$_2$O$_3$, GeO$_2$ are found to be electronic conductors. Denton [1954] was the first to observe semiconductivity in Vanadium phosphate glasses. The electronic conduction mechanism was very well discussed using Mott’s small polaron theory [Mott 1968]. He has also discussed about variable range hopping above 50K in some vanadium containing glasses. Greaves [1973] has suggested variable range hopping even at relatively high temperature. Vanadium glasses are semiconductors and their semiconducting nature arises due to the presence of two valence states of vanadium ions V$^{4+}$ and V$^{5+}$ [Austin 1969; Sayer 1972; Greaves 1973; Chung 1979, 1980]. Their electrical conduction processes occur due to the hopping of an unpaired 3d$^1$ electron from a V$^{4+}$ to a V$^{5+}$ site [Mott 1968; Austin 1969]. The unpaired electron induces a polarization of the vanadium ion and forms a polaron and this polaron hopping is responsible for conduction. Several work on vanado-arsenate glasses [Chung and Mackenzie 1980], vanado-germanate glasses [Khan 1984], vanado-bismuthate glasses [Ghosh 1987] and several ternary glass system have been reported in the literature. In all these glasses, the conduction occurs by hopping of electrons from low to high valence state of transition metal ion. Murawaski [1979] has reviewed the experimental work on binary semiconducting glasses and discussed the parameters viz. redox ratio (C), average hopping distance (R), exponential term [exp (-2αR)] and the activation energy (E$_a$). The dc conductivity behaviour of Boron-vanadate glasses was well described by El Mkami [2000] with the help of “small polaron” model. Using this model, physical parameters characteristic of the small polaron, $R$ and $W_{II}$ were evaluated. The results show that an adiabatic character is associated to the hopping.
2.5 (c) Frequency – dependent conductivity and dielectric relaxation in glasses

While there has been a large number of theories to interpret the observed dispersion behaviour of ion conducting glasses, the universal model for ac transport behaviour of glasses seems to be more successful. The first approach to describe the ac conductivity in these glasses were formulated by Jonscher [1977] who pointed out that ac conductivity of disordered materials is often found to follow a power law behaviour over a wide range of frequencies. The variation of ac conductivity $\sigma(\omega)$ with frequency is represented by the equation

$$\sigma(\omega) = \sigma(0) + A\omega^s$$  \hspace{1cm} (2.13)

where $\sigma(0)$ refers to the zero frequency conductivity and $s$ is the exponent which is of much significance to theories of ac conductivity. The expression has been widely used by Almond and West [1982, 1983 and 1984] in their analysis of ac conductivity data. However it has been observed that in several cases [Wong and Angell 1976] that the exponent ‘$s$’ in the power law increases with increasing frequency and approaches a value of unity. Hence a modified power law [Elliot 1994] of the following type has been proposed.

$$\sigma(\omega) = \sigma(0) + A\omega^{s_0} + A'\omega^{1.0}$$  \hspace{1cm} (2.14)

where $0 < s_0 < 1$. This finds support from the fact that ac conductivity of most glasses exhibits three linear or quasi – linear regions. The regions are the dc plateau where $\sigma(\omega)$ is a constant and equal to $\sigma(0)$, the Jonscher region where $\sigma = A\omega^s$ and a high frequency region where ‘$s$’ has a value of 1. This can be explained physically on the basis of a cluster –tissue texture of glasses [Ingram 1987]. Extensive measurements of
ac conductivity over wide range of temperature and frequency have shown that a single power law is inadequate to describe the dispersion of conductivities. Bruce [1985] investigated ionically conducting nitrate glasses and concluded that a double power law of the form

\[
\sigma(\omega) = \sigma(0) + A\omega^{s_1} + B\omega^{s_2}
\]  

(2.15)
describes the ac conductivity better than a single power law. The behaviour of the first region in the double power law equation can be described by the diffusion controlled relaxation model of Elliott [1989, 1994, 1988, and 1990].

The transition from \( s = 1 \) to \( s < 1 \) region with increasing temperature in equation (2.15) is also sensitive to the frequency window.

\( \varepsilon^* \) the complex permittivity, is considered as a fundamental parameter for the macroscopic description of a dielectric when exposed to the alternating fields. The electric modulus \( M^* \) is expressed as

\[
M^* = M' + jM''
\]

(2.16)

where \( M' \) and \( M'' \) are the real & imaginary parts of electric modulus. The electric modulus \( M' \) is defined by the reciprocal of the complex permittivity \( \varepsilon^* \) [Ross Macdonald 1987, 1992]. The complex electric modulus spectra represent a measure of the distribution of ion energies or configurations in the structure and describe the electrical relaxation in ionic glasses [Macedo 1972; Provenzano 1972]. The frequency range for which electric modulus \( M'' \) gives a good fit is found to be a proper window for determining \( s \) [Jain and Hsieh 1994]. Another approach of analysis of frequency dependent conducting behaviour was demonstrated by Kahnt [1991] using the master plot of \( \frac{\sigma(\omega)}{\sigma(\text{dc})} \) verses \( \frac{\omega}{\omega_0} \), where \( \omega_0 \) is the frequency corresponding to the maximum
dielectric loss. Barczynski et al [2002] has studied the comparison of the electrical properties of iron phosphate glasses containing different amounts of sodium ions and copper oxide glasses to other Transition metal oxide (TMO) glass systems. The influence of the role of transition metal oxide in the glass forming network on the electrical properties of glass has been outlined.

2.5 (d) Mixed conductivity

In glasses with high concentration of TMI and low concentration of alkali oxide, a ‘cross over’ from predominantly ionic to electronic conductivity takes place [Bazan et al 1996; Garbarczyk et al 1999]. There has been reports regarding Lithium vanadate-phosphate ternary glass system exhibiting mixed electronic-ionic conduction [Souquet 1990; Garbarczyk 2002], depending on the proportions of the constituents, which can be purely ionic (low V$_2$O$_5$ content), almost purely electronic (high amounts of V$_2$O$_5$) or intermediate electronic-ionic [Jozwiak et al 2005]. The relative ratio between the electronic and ionic components of the conduction can be controlled in a continuous way by appropriate changes in the glass composition. Ionic conduction in these glasses occurs via the motion of Li$^+$ ions, while electronic transport takes place by electron (polaron) hopping between V$^{4+}$ and V$^{5+}$ centres present in vanadate glasses. Electrical properties of glasses in the AgI–Ag$_2$O–V$_2$O$_5$–P$_2$O$_5$ system, which in general exhibit mixed electronic–ionic conduction were investigated by Machowski et al [2003]. The impedance measurement studies on higher vanadium content done by Barczyński [2006] et al have revealed that conductivity mainly depends on alkali and TMO concentration and two relaxation peaks connected with electronic and ionic transports were also observed.
2.6 Spectroscopic Characterization

The spectroscopic techniques provide a wide range of quantitative and qualitative information. Spectroscopic techniques work on the principle that under certain conditions, materials absorb or emit energy. Spectroscopic properties such as optical absorption and Electron spin resonance (ESR) investigations can be used as probes to identify the environments of the dopant ions and valence states in the host glass network. Infrared, Raman and Nuclear Magnetic Resonance (NMR) spectra throw light on the structural aspects of the glasses. Investigations on luminescence properties of glasses gives an idea to what extent the materials can be exploited as laser hosts by varying the environment of especially the rare earth ions in the glass network. Thus spectroscopic investigations namely optical absorption, ESR, IR, Raman and PL studies are useful in elucidating the scope for practical utility of these glasses.

2.6 (a) Infrared Spectroscopy

Infrared (IR) spectroscopy which is one of the most powerful analytical techniques has been most widely used to obtain structural information of glasses. This in turn provides information about principal building blocks present in the glass and local building arrangement. One of the most important advantages of infrared spectroscopy over the other usual methods of structural analysis like X-ray diffraction, Electron Spin Resonance, etc is that it provides useful information about the structure of the molecule quickly without tiresome evaluation methods. The utilisation of Infrared data in conjunction with other physical measurements, such as those obtained from Nuclear Magnetic Resonance and mass spectroscopy, can elucidate many facts about the structure and properties of the glasses. One of the fundamental requirements for the analysis of IR radiation is that there must be a net change in dipole moment
during the vibration of the molecule or the functional group under study. Previously recorded reference spectra can be used for identification by comparing it with the spectra of the unknown. The structural features are capable of producing characteristic and reproducible absorptions in the spectrum which in turn gives information regarding the linear or branched chain and functional groups, bending and stretching vibrations etc. Once detected, it helps in determining the local orientation of the group and its local environment or location in the structure. For example, in boro-vanadate glasses, the basic glass contains several borate and vanadate structural units in the glass network and when an alkali oxide such as Na₂O is added, O²⁻ take part in bond breaking and Na⁺ may reside interstitially. Such information about the changes in the basic glass structure that take place upon the addition of a cation can be studied from the IR spectra.

The IR spectra of glasses consists of absorption bands. The width of these bands have been attributed to distribution in bond angles and force constants due to the breakdown of vibrational selection rules [Gaskel 1979]. Alben et al [1975] also suggested the usefulness of this technique to study glasses possessing heteropolar bonds. The signature of a particular vibrational mode in such glasses may result from the change in dipole to a heteropolar bond, which occurs because of the atomic displacements. The IR spectra of glasses containing phosphorus and vanadium have been extensively studied by Muller [1969] and Osaka [1984]. They showed that phosphate glasses mainly consist of corner shared PO₄ groups. Dimitriev and co-workers [1983] reported that the IR spectra in vanadate glasses consist of VO₄ units. The structural anomaly of boron in alkali and alkali earth borate glasses qualitatively supports the model of Krogh Moe [1965], according to which the coordination of boron changes from 3 to 4 by the addition of modifier oxide. El-Ahdael et al [2011] investigated Lead-Phosphate glasses doped with MnO₂ and concluded that the IR
absorption spectra indicates the presence of the characteristic phosphate structural chains, mostly as metaphosphate units, and the MnO₂ ions seem to cause some depolymerization effect. Muthupari et al [1994] synthesized sodium boro - vanadate glasses by melt quench method and found that modification results in the formation of tetrahedral B₄ units in the structure and IR spectroscopic results are consistent with the formation of diboro- vanadate species. Therefore various bands present in IR spectrum correspond to the characteristic functional groups present in a chemical substance. Thus an IR spectrum of a chemical specimen is a finger print for its identification.

2.6 (b) Raman Spectroscopy

Another form of vibrational spectroscopy is Raman spectroscopy, which is complementary to infrared spectroscopy. A net change in bond polarizability is necessary for a transition to be Raman active. Raman spectroscopy deals with the scattering of light and this technique is used to observe vibrational, rotational, and other low-frequency modes in a system. Certain diatomic molecules like H₂, N₂, O₂, etc which do not possesses a permanent dipole moment will not show IR spectra but show Raman spectra since their vibration is followed by a change in polarizability of the molecules. There occurs a change in the induced dipole moment at the vibrational frequency as a result of the change in polarizability. Vibrational spectroscopy such as Raman scattering is one of the powerful techniques used for materials characterization [Huang et al 1996; Inaba et al 1997; Julien 1998, 1999, and 2000]. As it is sensitive to amorphous components and those with short-range order, Raman Scattering yields a more complete and reliable description of disordered materials.

Kamitsos et al [1987] analyzed the Raman and infrared spectra of magnesium-sodium-borate glasses in order to elucidate the role of MgO in such glasses. The results
obtained for both the spectra were complementary to each other. Raman spectroscopy was quite effective in probing formation of non-bridging oxygen containing pyro- and metaborate units, but not so effective in showing the existence of small amounts of boroxol rings in the high oxide content where as IR showed clearly the destruction of diborate groups and the formation of boroxol rings but gave no clear picture for the nature of the non-bridging oxygens containing borate groups. Raman studies indicated high degree of cross linking for silver–vanadate–phosphate glasses [Garbarczyk et al 2000]. Chandkiram Gautam [2012] studied the optical properties of boro-silicate glasses doped with lanthanum oxide glass samples using Infrared (IR) and Raman spectroscopic methods. IR measurements were recorded over a continuous spectral range 200 - 4000 cm$^{-1}$ to study their structural arrangement, while Raman spectra were done over a continuous spectral range 200 - 2000 cm$^{-1}$. Infrared spectra of all glass samples showed a number of absorption peaks which occurs due to asymmetric vibrational stretching of borate by relaxation of the bond B-O of trigonal BO$_3$. The Raman spectra exhibited different spectral bands and intensity of these bands were found to change remarkably for all glass samples. In the present study, the Raman spectroscopy has been used for identifying various structural units like phosphate, borate and manganese, etc in the glass matrix and the changes occuring in the structural units with the varying concentration of modifier oxides.

2.6 (c) Nuclear Magnetic Resonance Spectroscopy

Nuclear Magnetic Resonance (NMR) is a branch of spectroscopy in which radio frequency waves induce transitions between magnetic energy levels of nuclei of a molecule. NMR is another powerful tool for investigating molecular structure and is used for understanding mainly the structure and dynamics of nucleus. It makes use of
the lifting of degeneracy of spin states of a nucleus having non-zero spins in the
presence of magnetic field. Silver and Bray [1958] were the first one to highlight the
role of NMR in the study of borate glasses and reported the work on $^{11}$B wide-line
NMR spectra of several commercial borate glasses. The structural models of borate,
borosilicate, and aluminoborate glasses could be developed on the basis of $^{11}$B NMR
data. Besides this, many glasses which contain quadrupolar nuclei with spin numbers
such as $^{11}$B (3/2), $^{23}$Na (3/2), $^{27}$Al (5/2), etc have been characterized using solid state
NMR [Goebel et al 1979; Mueller et al 1981; Turner et al 1987; Bray et al 1988]. In
addition to the magnetic dipole moment, nuclei with spin greater than $\frac{1}{2}$ possess
electric quadrupole moment (eQ). This eQ can interact with the electric field gradient
(eq) around the nucleus and gives rise to a set of energy levels. In the conventional
NMR experiments, the effects of quadrupole interaction come to the surface as
perturbations. These perturbations can split the resonance line into several components.
The number of components, their frequency separation, the broadening and the intensity
of resonance lines give valuable information about the environment of the nucleus such
as molecular structure and bonding. Fig 2.9 represents the quadrupolar spectra of $^{11}$B
nucleus with spin 3/2 [Lee et al 1997]. In the figure, the first order quadrupolar
interaction is visible with a sharp central transition and various satellite transitions are
present symmetrically on both sides of the central transition. Here $\nu_0$ is the Larmor
frequency and $\nu_Q$ the quadrupolar frequency and $\nu$ the fixed frequency. The central
line changes depending on the quadrupole coupling constant $Q_{cc}$, the asymmetry
parameter $\eta$, and the resonance frequency which depends on the external static
magnetic field.

The separation of the two peaks from the central line decreases with increasing
resonance frequency. B$_2$O$_3$ glass usually contains BO$_3$ units, but on addition of alkali
oxide BO₃ units get converted to BO₄ configuration and generate an overlapped NMR absorption line (Fig. 2.10) from both the BO₃ and the BO₄ coordinations.

![Diagram showing spectra of a Quadrupolar nuclei with spin 3/2](image)

**Fig. 2.9. Spectra of a Quadrupolar nuclei with spin 3/2 [Lee et al 1997].**

Yun (1978) described the method of calculating the fraction N₄ of borons that where in BO₄ units from the NMR absorption curve of, as shown in Fig. 2.10, by taking the ratio of the area B₄ under the narrow portion (from the BO₄ units) to the total area B₃+B₄ under the curve. The central line shape of BO₄ mainly depends on the nuclear quadrupole coupling constant \((e^2qQ/h)\), the asymmetry parameter (\(\eta\)), and the resonance frequency (\(\nu_0\)) which in turn depends on the external static magnetic field (H). Resonant absorption takes place, when energy corresponding to the energy difference between allowed pair of the \((2I+1)\) Zeeman split levels (where ‘I’ is the nuclear spin quantum number) of the nucleus is supplied to the system. Abragam [1961] and Fyfe [1983] expressed a general Hamiltonian for the interactions experienced by a nucleus of spin ‘I’ in solid state in terms of Zeeman interaction, dipole-dipole interaction, chemical shift interaction and quadrupolar interaction.
All the above interactions are in general, anisotropic and yield different values, depending on the orientation of the local symmetry axes of the resonating nucleus to the applied field and due to this the NMR resonance signal in glasses are usually very broad. NMR studies on phospho-vanado alkali system prepared by melt quenching method studied by Ryszard J Barczyński et al [2008] revealed a systematic change in shape with increase in alkali content and were correlated as due to change in vanadium structural unit.

2.6 (d) MAS NMR Spectroscopy

The NMR lines in glasses are generally broad, mainly because of the inherent structural disorder. As a result, chemical inequivalent sites go undetected. Andrew and Lowe [1959] had reported that Magic Angle Spin (MAS) can effectively suppress the anisotropic contributions. High resolution NMR in solids by magic angle spin (MAS) has evolved as a powerful method for obtaining well resolved NMR lines in
solids [Fyfe 1983]. Spinning causes an averaging out of coordinate dependent quantities. For example, dipole-dipole interaction and first order quadrupolar interaction involve a term $(3\cos^2\theta - 1)$. When the sample spins about an axis which is inclined at an angle of $54^044'$ to the external magnetic field, the anisotropic contributions in dipolar Hamiltonian vanish and the average value of $(3 \cos^2 54^044' - 1)$ is zero. The chemical shift is also reduced to the isotropic value. Thus, spinning suppresses effects of both homo-nuclear and hetero-nuclear dipolar interactions and first order quadrupole interactions, thereby narrowing the otherwise broad resonance. Hence, sharp peaks corresponding to the isotropic chemical shifts are observed, along with a series of side bands on either side and separated by the sample spinning frequency [Andrew 1966, 1981]. This spectroscopic technique is of course most useful analytically, because it allows better resolution and therefore better measurement of chemical shift and spin-spin splitting. Thus, MAS NMR spectroscopy not only gives information about the local structure of a particular atom, but also gives an understanding of the dynamics of mobile ions in glasses through the so-called motional narrowing effect which occurs when the temperature is increased. Muller-Warmuth et al [1982] have determined the activation energies for lithium ion motion in glasses with the help of $^7$Li NMR. Scott Kroeker et al [2001] investigated a series of anhydrous, polycrystalline, binary borates with the help of $^{11}$B MAS NMR, to obtain precise measurements of their three-coordinate boron isotropic chemical shifts.

2.6 (e) Electron Paramagnetic Resonance (EPR) Spectroscopy

EPR is one of the important resonant spectroscopy, in which radiation having frequency in the microwave region is absorbed by paramagnetic substances, which have spin degenerate ground states to induce transitions between magnetic energy levels of electrons with unpaired spins. This is employed to understand the symmetry of
surroundings of the paramagnetic ion and the nature of the bonding to the nearest neighbouring ligands.

When microwave frequency ($\nu$) is applied perpendicular to the direction of the field, resonance absorption will occur between the two split spin levels and the resonance condition is given by,

$$h\nu = g\mu_B H,$$  

(2.17)

where ‘$h$’ is Planck’s constant, ‘$g$’ is the spectroscopic splitting factor and ‘$\mu_B$’ is the Bohr magneton. From equation (2.17), it is quite evident that the resonance condition can be satisfied by varying ‘$\nu$’ or ‘$H$’ and hence EPR studies are carried out at a constant frequency ($\nu$) by varying magnetic field (H). Since $h$ and $\mu_B$ are constants, one can calculate the g factor and this factor determines the divergence of the Zeeman levels of the unpaired electron in a magnetic field and is characteristic of the spin system [Lund et al 2011]. For a free electron, the $g$ value is 2.0023. In a magnetic field $H$, there are two energy states of unpaired electron as illustrated in Fig. 2.11. Chemical shift in the NMR spectra is quite similar to the hyperfine splitting in EPR spectra, because both are caused by the interaction between adjacent spinning magnetic field and spinning electrons.

Fig. 2.11. Splitting of energy level of a free unpaired electron in magnetic field
The number of splitting will be $2I+1$, where ‘I’ is the spin quantum number when a single electron interacts with a nucleus. Thus in general, if a single electron interacts magnetically with ‘n’ equivalent nuclei, the electron signal splits up to $(2nI+1)$ multiplet. EPR is usually presented as derivative curves. The first derivative (the slope) of the absorption intensity (I) is plotted against field strength (H) and Fig.2.12 shows two schematic representations of absorption and its derivatives. EPR has limited applications because it is observed primarily in systems containing unpaired electrons.

Fig. 2.12. Schematic representation of ESR absorption and its derivatives

Harry et al [1967] reported hyperfine structure constants of vanadium using EPR spectra. Sunandana and Bhatnagar [1984] interpreted hopping conduction with the help of EPR spectra in the temperature range of 298–498 K for V$_2$O$_5$ - MO$_2$ glasses (M= Ge, Se,Te) and observed progressive broadening and eventual disappearance of the hyperfine structure with temperature. This is attributed to the delocalization of 3d$^1$ electron spin leading to hopping conduction and have found covalency of the V - O bond to increase from GeO$_2$ to TeO$_2$ to SeO$_2$. Cozar et al [2001] had a detailed
structural study of Lithium boro-vanadate glasses with the help of EPR spectra and came to the conclusion that vanadium ions occurs in both $V^{4+}$ and $V^{5+}$ valence states. Agarwal [2003] has reported about use of vanadyl ion ($VO^{2+}$) as a spectroscopic probe for characterization of glasses, as their EPR spectra are found to be rich in hyperfine structures due to $^{51}V$ and is easily observable at room temperature. Optical absorption, EPR and IR spectral studies on $Li_2O–Na_2O–B_2O_3–Bi_2O_3$ by Srinivas et al [2006] have confirmed the presence of BO$_4$ and diborate local structures and a single absorption band in the near infrared region. Anshu et al [2008] synthesized vanadyl doped tungsten lithium borate glasses and recorded the first derivative of EPR. The results were found to convey the presence of hyperfine interaction arising from an unpaired electron with a $^{51}V$ nucleus having nuclear spin 7/2.

The EPR and optical absorption spectra of vanadyl ions doped in alkali calcium borate glasses have been interpreted as being due to the presence of six coordinated tetravalent vanadium [Sreekanth Chakradhar et al 2000]. The spectral properties of mixed alkali potassium borate glasses doped with manganese ions were also investigated by Sreekanth Chakradhar et al [2003] using EPR and optical absorption techniques as a function of alkali content. The EPR spectra exhibited resonance signals which are characteristic of the Mn$^{2+}$ ions and the resonance signal at $g \sim 2.02$ exhibited a six line hyperfine structure.

2.6 (f) Optical Spectroscopy

Optical spectroscopy has been considered as one of the important analytical tool for studying the nature of glasses, especially to find the potential applications in the production of optical components and commercial filter glasses. It is one of the beneficial tools used to figure out the electronic structure of amorphous materials.
The optical absorption spectra are usually recorded using UV-VIS spectrophotometer. According to Mott et al [1971] and Altaf et al [2003], the standard method usually employed for investigating the optically induced electronic transitions in materials is to measure the optical absorption coefficient (α) near the fundamental absorption edge. Usually two types of transition namely the direct and indirect transitions occur at the absorption edge. The absorption coefficient can be determined for different wavelengths using the relation [Sindhu et al 2005].

\[
\alpha(\nu) = \left( \frac{1}{d} \right) \ln \left( \frac{I_0}{I_\nu} \right)
\]

where ‘I₀’ and ‘Iₙ’ are intensities of the incident and transmitted beams and ‘d’ corresponds to thickness of sample. Davis and Mott [1970] gave the absorption coefficient α(ν) as a function of photon frequency (hν), for direct and indirect transitions using the relation [Abdel- Baki et al 2006].

\[
\alpha(\nu) = B (h\nu - E_{\text{opt}})^n / h\nu
\]

where the exponent \( n = 1/2 \) for an allowed direct transition, \( n = 2 \) for an allowed indirect transition and ‘B’ is a constant.

The optical energy band gap (\( E_{\text{opt}} \)) for indirect and direct transitions can be found, by plotting \( (\alpha h\nu)^{1/2} \) and \( (\alpha h\nu)^2 \) as a function of photon energy (Tauc’s plot). The respective values of \( E_{\text{opt}} \) are obtained by extrapolating \( (\alpha h\nu)^{1/2} = 0 \) for indirect transitions and \( (\alpha h\nu)^2 = 0 \) for direct transitions [Sreekanth Chakradhar et al 2003].

Subrahmanyam et al [2000] has calculated the Urbach energy values (ΔE), by taking the reciprocal of the slopes of the linear portion in the lower photon energy region, of the plot of logarithm of absorption coefficient and function of photon energy as stated in the relation

\[
\alpha(\nu) = \alpha_0 e^{hv/\Delta E}
\]
Dimitrov et al [2002] proposed that the refractive index of the glasses can be calculated using the relation

\[
\left( \frac{n^2 - 1}{n^2 + 2} \right) = 1 - \sqrt{\frac{E_g}{20}}
\]  

(2.21)

According to Klinokowski [1985], the electron polarizability \( \alpha_0 \) can be calculated using the relation

\[
\alpha_0 = \frac{3 (n^2 - 1)}{4\pi N(r_d^2 + 2)}
\]  

(2.22)

Duffy and Ingram [1975] reported that the optical basicity of an oxide glass which reflects the ability of the glass to donate negative charges to the probe ion can be estimated using the relation

\[
\Lambda_{oh} = \sum_{i=1}^{n} \frac{Z_i r_i}{2\nu_i}
\]  

(2.23)

where ‘n’ is the total number of cations present, ‘\( Z \) ’ is the oxidation number of the \( i^{th} \) cations, ‘\( r_i \)’ is the ratio of \( i^{th} \) cations to the number of oxides present and ‘\( \nu_i \)’ is the basicity moderating parameter of the \( i^{th} \) cation. The basicity moderating parameter ‘\( \nu_i \)’ can be calculated using the following relation put forth by Duffy and Ingram[1975]

\[
\nu_i = 1.36 (x_i - 0.26)
\]  

(2.24)

where ‘\( x_i \)’ is the Pauling electronegativity [Pauling 1960] of the cation.

The transitions can be observed from the optical absorption spectra and the assignments of these transitions can be made following Carnall et al [1968]. The experimental oscillator strength (\( f_{meas} \)) of the absorption transitions has been calculated using the relation

\[
f_{meas} = 4.32 \times 10^{-9} \int_{\nu_i}^{\nu_s} \epsilon(\nu) d\nu
\]  

(2.25)
where $\varepsilon(\nu) = \text{OD} / \text{ct}$ is the molar extinction coefficient, ‘OD’ being the optical density, ‘c’ the concentration in moles/Lt and ‘t’ the optical length of the glass in ‘cm’. The theoretical oscillator strengths can be calculated by using Judd–Ofelt theory [Judd 1962; Ofelt 1962]. Karthikeyan et al [2005] had reported the optical and non-linear optical properties of Neodymium doped heavy metal borate glasses, using the theory of Judd–Ofelt. Borate glasses containing single and mixed transition metal oxides were investigated by Bandyopadhyay et al [1981] with the help of Optical and ESR spectra and concluded the presence of all valence states of two TM elements. Karthikeyan et al [2003] investigated structural, optical and glass transition studies on Nd$^{3+}$ doped lead bismuth borate glasses and revealed that addition of Nd$_2$O$_3$ in the host glasses does not make significant change in the glass transition temperature. The optical studies showed that this glass has low asymmetry in the rare earth ion site and these glasses are suitable as laser materials. The effect of the rare earth ion concentration on the physical and optical properties of Neodymium doped Soda-Lime-Silicate glasses have been studied by Parnuwat Chimalawong et al [2012] using the UV absorption spectra and the indirect optical band gaps have been evaluated. The optical band gap has been found to decrease with increasing Neodymium concentration.

### 2.6 (g) Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is a contactless, non-destructive method to probe the electronic structure of materials. It is one of the kinds of luminescence phenomenon, where the emission of optical radiation results from various types of excitation namely, chemical or biochemical changes, electrical energy, subatomic motions, reactions in crystals or stimulation of an atomic system, etc [Newton Harvey 2005]. The analysis of the PL signal derives information on the emitting material and
is particularly useful in surface diagnostics, because the phenomenon often originates from the surface layers of the material [James 1983]. Investigation of rare-earth–doped glasses using PL techniques helps in the development of optical communications and in the increase of bandwidth capacity of optical fibre systems. Kesavulu et al [2009] reported that PL spectra of Lithium-Potassium Borophosphate glasses doped with Mn$^{2+}$ ions exhibited a green emission peak which is attributed to a transition from excited $^4T_{1g}$ to the ground $^6A_{1g}$ state of Mn$^{2+}$ ions. Annapurna et al [2003] synthesized Zinc-borosilicate glass containing Nd$^{3+}$ ions to study the NIR fluorescence and the violet up conversion emission properties. NIR photoluminescence spectrum has been recorded with the 514 nm line of Ar$^+$ laser to observe emission lines. Ning Da et al [2010] reported intense red fluorescence from Mn$^{2+}$ doped sulpho-phosphate glasses using the PL spectra. Photoemission was found to occur at around 620 - 650 nm with a bandwidth of $\sim$110 nm and emission red-shifted for increasing Mn$^{2+}$ concentration, and blue-shifted for increasing ratio of SO$_3$:P$_2$O$_5$. The increase in dopant concentration was responsible for the linear increase in emission intensity. Madhusudana Rao et al [2013] studied extensively the PL spectra of Lithium sodium borate glasses doped with different concentrations of V$_2$O$_5$ recorded at 254 nm excitation wavelength at room temperature and the luminescence spectra was found to exhibit two sharp peaks at 370 nm and 470 nm.

2.7 Applications of Oxide glasses

Work on borate, phosphate, vanadate and neodymium glasses have been carried out by researchers during the past several decades, especially pertaining to the optimization of glass preparation and investigations on their physical, thermal, structural and optical properties in view of the technological applications of glasses.
Wong et al [1976] found that glasses containing vanadium pentoxide have many important applications in the field of solid state electronics. Vanadate glasses are known to demonstrate semiconducting properties [Mott 1968]. Taylor [1977] reported that vitreous V₂O₅ based materials can be used as cathode materials for lithium based batteries. B₂O₃ is a good glass former and is a primary component of many large volume industrial glasses including those used in nuclear waste storage [Griscom 1980; Plodinec 2000; Maniu 2001]. Authors [Ingram 1987; Tuller et al 1988 and Agarwal et al 1999] have reported about technological importance of glasses with high ionic conductivity because of their potential application as solid state electrolytes. Ionic conducting glasses are found to have many advantages over the crystalline or polycrystalline materials [Liebert 1976; Angell 1986; Souquet 1995]. Sakurai et al [1985] reported that glasses of the phosphate, borate, vanadate and telluride families could be used for photonic applications. Weeks [1974] and Venkata Subba Reddy [2009] mentioned that the glasses containing transition metal ions have attracted researchers due to their physical applications in electrochemical, electronic and electro-optic devices. Kreidl et al [1990] pointed out that glasses doped with transition metal ions came into prominence because of their notable spectroscopic properties as well as their suitability for optical communications and luminescent solar energy concentrators. Glebov et al [2000] focussed on glass systems containing transition metal ions because of their use as photoconducting devices, magnetic materials etc.

Literature surveys [Misra et al 1983; Strach et al 1984; Rubins et al 1989; Pasimeni et al 1993; Pandey et al 1999] have reported about Mn²⁺ ion, a d⁵ high-spin ion, widely used as an extremely powerful EPR probe in the study of structural as well as dynamic aspects of crystalline state by incorporating it in diamagnetic crystals. Masaru et al [2004] synthesized lead-phosphate glass systems containing manganese
ions to probe the glass structure and reported that manganese ($^{55}$Mn) ions have been frequently used as paramagnetic probes to explore the structure and properties of vitreous systems. Manganese ions have a strong bearing on the optical and magnetic properties of the glass. Tischendorf et al [2001] presented an overview about zinc phosphate glasses used in manufacturing glass polymer composites, optical, waveguides and solid state laser sources. These glasses are used as solders and welds between glassy and metallic parts in Television tubes and electronic circuits, as their thermal expansion coefficients are similar to that of many metals. According to Sreekanth Chakradhar et al [2003], a large number of interesting studies are available on the environment of manganese ion in various inorganic glass systems.

Pure phosphate glasses were not considered for industrial and technological applications due to their hygroscopic nature and volatility. But, the recent developments of novel compositions of these glasses with superior physical and chemical properties of these glasses have revived interest in phosphate glasses. Wells (1975); Proulx (1994); Rao (2002) and Prasad (2005) have reported that phosphate based glasses are both scientifically and technologically important materials as they offer some unique physical properties because of the linked PO$_4$ structural units with covalent bonding in chains or rings. These glasses are used in various applications such as bone transplantation [Oliveira et al 2000], glass to metal seals [Brow et al 1995, 2000; Wei et al 2001], containment of radioactive wastes [Sales and Boatner 1986], fast ion conductors [Kokubo et al 1986], laser host materials [Weber 1990], etc.

Levy et al [1989] reviewed the work on rare earth doped glass and pointed out that these glasses are found to be efficient compact laser devices. During the last decade, doped materials are interesting and technologically relevant subject of research because of their unique optical properties and potential applications. Rare earth ions
used as dopants in glasses are found to have applications mainly because of their well-defined and sharp energy levels that serve as structural probes for the environment of the dopant. Besides, the modifications of the energy level structure of the rare earth ions which are caused by the glassy environment may lead to interesting applications [Gatterer et al 1998; Pisarski et al (2005)].

2.8 Motivation and Objective of the Thesis

Many properties of the glass depends on the chemical composition. Compositional species in glass can be categorized depending on the concentration of network formers, modifiers and intermediate species. So, proper selection of modifiers and formers in the glass composition leads to the formation of glass with unique properties. The dc and ac electrical conductivity analysis and their measurements on ion conducting glasses are found to be a field of major interest. The measurement of the ac conductivity on ion conducting glasses over a wide range of frequencies and temperatures is a valuable tool for determining the ion dynamics or relaxation process. Variation of concentration of alkali and transition metal oxide in the glass system leads to a transition from ionic to electronic through mixed ionic - electronic conduction. Compositions of glass with high alkali and low vanadium content are reported to exhibit pure ionic conduction whereas, high vanadium and low sodium content glasses were reported to be electronic conductors. The changes in the nature of the electrical conduction produce changes in the characteristic features of impedance spectra. But at a moderate composition of sodium and vanadium ‘a crossover’ from ionic to electronic is observed and therefore it is an interesting area of study. The bulk conductivity and the electrical behavior of the glass system can be obtained from impedance analysis. Although transport, elastic and structural studies have been reported [Muthupari et al 1995] on sodium boro-vanadate glass systems by melt quench techniques, sufficient
information is not available on such systems with higher and lower levels of vanadium concentration. It is of interest to investigate these properties at the extreme levels of concentration in sodium boro-vanadate glasses by the novel microwave method. As the structural motifs can be used to explain various changes seen in the transport, thermal and physical properties. Detailed studies on spectroscopic properties namely optical absorption, NMR, Infrared, Raman and ESR properties of glass system containing transition metal ions are expected to throw more light not only on structural aspects but also on the suitability of these materials in a variety of electrical and optical devices.

In the present study, sodium phospho-zinc glass system doped with various concentrations of manganese has been taken up to get a clear picture of dopant induced effects on optical absorption and photoluminescence. The fundamental optical band gap of the glasses can be computed based on their optically induced transitions.

In recent times, glasses doped with rare earth ions have attracted a considerable interest due to their photonic applications as optical amplifiers and solid-state lasers. Neodymium is one of the most studied rare earth ion and is found to have immense applications in photonic devices [Gatterer et al 1998]. It is found that not much work is reported on the effect of doping with neodymium in sodium phospho-zinc glass system. The addition of an extra cation to the glass network exerts influence on the glass structure leading to the creation of non-bridging oxygen, which leads to the depolymerization of the network. This work is undertaken with the aim of investigating the effect of Nd₂O₃ content on the optical band gap, density, molar volume, optical basicity and polarizability in sodium phospho-zinc glasses synthesized by microwave method.
Synthesis of the glasses have been carried out using microwave heating technique. Microwave heating is fundamentally different from conventional heating [Sutton 1989]. In the conventional heating methods, undesirable decomposition, oxidation / reduction of reactant oxides, loss of material by evaporation due to long processing time may give inaccurate results, whereas in the microwave processing it is possible to achieve rapid and uniform heating. In this process, the only requirement is that at least one of the components used for synthesis of glass, must be a microwave susceptor [Rao K J et al 1995]. Hence environmental friendly heating process was adopted for synthesizing glasses to study thermal, transport and spectroscopic properties of glasses.

For the present study, the chemical compositions of the three glass systems synthesized using microwave route are:

1. system \([(100 – x) 0.5( Na_2O – B_2O_3 ) – x V_2O_5] \ (where \ 10 \leq x \leq 50 \text{ mol \%})

2. system \([(80 – x) NaPO_3 – 20 ZnO – x MnO_2] \ (where \ x = 1, 3, 5, 7.5, 10 \text{ mol \%})

3. system \([(80 – x) NaPO_3 – 20 ZnO – x Nd_2O_3 ] \ (where \ x = 0, 0.1, 0.3, 0.5, 0.7 \text{ mol\%})

with the objective of studying

i) Transport properties mainly electronic, ionic and mixed conductivity in sodium boro – vanadate glass systems

ii) Mechanical and thermal properties in relation to local structures.

iii) Spectroscopic analysis to elucidate several structural units formed due to network modification.
iv) EPR measurements to study vanadium environment in sodium boro–vanadate glasses and manganese environment in sodium phospho-zinc oxide doped manganese glasses.

v) Optical and photoluminescence properties of sodium phospho–zinc oxide glasses independently doped with manganese and neodymium.