CHAPTER-1

INTRODUCTION

1.1 General Background

Glass is an amorphous solid that has been around in various forms for thousands of years and is one of the oldest synthetic materials used by the mankind. The beginning of 19th century saw an extensive scientific study on glasses by Faraday and others [Newton 1985]. All this work led to the development of glass science, which is a well-developed subject today and many new materials in amorphous forms of considerable technological applications have been prepared.

The term 'glass' refers to a “supercooled liquid” which is usually produced when a viscous molten material is cooled rapidly to a temperature below its glass transition temperature, with insufficient time for formation of regular crystal lattice. Here the disorder is frozen by the use of a suitable thermodynamic process; the disorder may be in position, connectivity, molecular orientation, spin, or any such property [Shelby 2005]. Conventional glass is a solid obtained by quenching from the molten state. It is a physical process in which enthalpy is rapidly removed from the system so that crystallization is bypassed. Numerous methods are now known by which crystalline solids can be amorphized. Industrial glasses are usually made by melting together four ingredients namely sand, soda ash, limestone, and cullet (to lower the melting temperature) [Jo Marshall 1990]. A key feature is that glasses have structures that are liquid-like i.e. non-crystalline. The non-crystalline materials that are also called amorphous are the ones in which the very arrangement of atoms or molecules is not regular and periodic.
Amorphous solids lack ordered long range arrangement compared to its crystalline counterpart, which have an ordered long range arrangement of atoms or molecules within the structure. However they may have a short range order due to chemical bonding. Experimental evidences suggest the presence of short or intermediate range of order up to 100 Å [Gaskell et al 1979, Bursill et al 1981]. The amorphous material is still a solid with molecules closely packed and chemically bonded. Fig. 1.1 represents the schematic representation of the same composition of ordered crystalline form and random amorphous network. Since glass lacks periodic atomic arrangement and long rage periodicity, it has higher configurational entropy and free energy as compared to its crystalline counterpart. In other words, a glass is a thermodynamically metastable material which remains untransformed to its stable state.

![Schematic representation of (a) crystalline form and (b) amorphous form of the same composition.](image)

The information about the structure of the glass system can be obtained from the X-ray and spectroscopic studies. X-ray diffraction pattern of glasses are usually
diffuse and consists of broad humps rather than sharp peaks as in case of crystalline solids. Consequently, the diffusion pattern can be used only to determine the amorphous nature but nothing can be said about the chemical composition. In view of the practical applications, the study of non-crystalline materials is very important.

In general, glass is a metastable state and possesses excess of enthalpy retained during quenching from liquid state [Richard Zallen 1983]. Thus glass can crystallize irreversibly and exothermally in many instances. However, because of the ability of several glasses to persist indefinitely below glass transition temperature, a glass can be prepared by supercooling a melt. They can be distinguished from other crystalline solids by the existence of unique thermal transition known as the glass transition temperature.

1.2 Glass Transition

As a glass forming liquid is cooled some of its properties such as specific volume, heat capacity and thermal expansivity change sharply in a narrow range of temperature. The temperature corresponding to the transition from a viscous liquid to a solid glass is called the glass transition ‘T_g’. If a glass is heated to a temperature above its glass transition temperature, there are chances for a reversible transformation (from a glass to a viscous liquid) to take place. Increase in viscosity is usually the reason for glass transition. Even though the chemical composition of the glass is the same, the glass transition may not always be the same as T_g depends on the cooling rate. A slow cooling rate allows enough time for a viscous liquid to change its local arrangement to attain the minimum free energy at the corresponding temperature, where as a rapid cooling causes an increase of viscosity that is too quick for the local atomic arrangement to follow and thus it results in a glass transition at
higher temperature. Glass transition exhibits features similar to those in second order
phase transitions in crystalline solids [Rao C N R and Rao K J 1978]. For instance,
thermodynamic quantities such as heat capacity ($C_p$), thermal expansivity ($\alpha$) and
volume compressibility ($\beta$) undergo discontinuous change at the glass transition.

1.3 Glass Formation

Glass can be formed from materials in which the nature of bonding can be of
several types such as ionic, covalent, metallic, Van der Waals and hydrogen (bonds)
or a combination of them. To understand glass formation, one has to consider not
only the structural aspects of the glass forming material but also the kinetic factors,
since a glass forming melt inevitably has to have a low rate of crystallization
compared to its rate of cooling. Several approaches have been adopted to arrive at a
common basis for glass formation. Glass forming tendency of a substance seems to be
related to how well the crystallization process can be suppressed in the melt. The
three–dimensional random network of strong bonds is obtained by the constituent
called the network former which consists of oxides such as germanates, silicates,
phosphates, borates, arsenates etc. These elements with intermediate electronegativity
can readily form glasses on their own when their melts are cooled and are also
commonly known as 'glass formers'. But certain oxides like vanadates, molybdates,
tungstates etc cannot form glasses on their own, but each will do so in conjunction
with another glass former, hence they are known as 'conditional glass formers'
[Rawson et al 1956]. There are some alkali oxides like $\text{Na}_2\text{O}$, $\text{Li}_2\text{O}$, $\text{K}_2\text{O}$ etc which
when added to the glass network forming oxides produce drastic changes in the
properties like melting point, conductivity etc. Such oxides which modify the network
structure of the glass are termed as 'network modifiers' [Rao K J 2002]. Dopant salts
are generally ionic halides that cannot interact with the macromolecular chains, but
remain dispersed without any modification of the glass structure and contribute to the ionic conductivity [Minami et al 1983]. Thus wide variety of multi-component glasses of desired composition can be prepared by changing the chemical composition. The complex chemical components of a glass are as a result of mixing of network former, network modifier and a dopant salt in different proportions. Glasses consisting of more than one components are enormous in nature and multicomponent systems are found to form glasses more easily.

1.4 Glass Preparation

Different techniques have been used for the synthesis of glassy materials. The various techniques used for the preparation of amorphous glassy materials include Thermal evaporation, Sputtering, Glow discharge, Thermal decomposition, Chemical vapor deposition, Electrolytic decomposition, Reaction morphisation, Melt quenching technique, Sol gel technique etc [Chandra 1981; Richard Zallen 1983; Rodrigues et al 1985; Cusack 1987; Kudo et al 1990; Elliot 1990 ; Drabold et al 2001]. Fig.1.2 shows various types of melt quench techniques used to prepare glasses [Mamata Chaudhuri 1983]. Glass is prepared by removing enthalpy of molten liquid sufficiently quickly. The cooling must be sufficiently fast to preclude crystal nucleation and growth. The crystallization rate of an under cooled liquid depends on the rate of crystal nucleation and on the speed with which the crystal-liquid interface moves. Therefore glasses are conventionally prepared by melt quenching technique. Various types of materials can be prepared in amorphous /glassy form using melt quench technique because of the ease of preparation and handling. Among these, the most widely used is the melt quench method using muffle furnace. Temperature controlled muffle furnace models are used in the temperature range from 100°C to 1800°C.
Microwave ovens can be used in processing of glasses [Sutton 1989]. There is a fundamental difference between microwave and conventional heating techniques. In conventional heating, heat transfer mechanisms like conduction, convection and radiation are responsible for transferring thermal energy to the material. The thermal energy is delivered to the material surface by convection heating and is then transferred by conduction to the bulk of the material. As an all-round heating takes place heat flows inwards into the material and a thermal gradient develops with the surface at higher temperature compared to the centre of the material. In microwave heating, however electromagnetic waves penetrate the material, gets absorbed and is directly converted to heat energy throughout the exposed/absorbing body. Since microwaves can penetrate and supply energy to the material, heat is generated...
throughout the volume of the material and results in a uniform and volumetric heating of the material. The schematic representation of conventional and microwave heating processes are shown in Fig. 1.3.

![Schematic representation of conventional and microwave heating patterns.](image)

**Fig. 1.3. Schematic representation of conventional and microwave heating patterns.**

In conventional processing methods of materials like ceramics and polymers, the processing time is very long because of the slow heating rate since they are not very good conductors of thermal energy. This long processing time often induces material fractures due to thermally induced stresses developed within the material. In contrast, microwave energy is delivered to the material by interaction of electromagnetic field at molecular level. Because of this reason, thermal stress which are developed in the material are significantly lower and insufficient to cause fracture of the material and therefore microwave processing is inherently faster. Further, microwave heating is also energy efficient compared to conventional heating because environmental heating is minimized [Rao K J et al 2002].
Ability of microwaves to convert electromagnetic energy into heat often depends on the physical state of the material with which it interacts. For example, water in frozen condition is microwave transparent whereas in the form of liquid it’s a very good microwave absorber. Different forms of carbon exhibit wide differences in their microwave response. Materials having different dielectric properties when in contact with microwave energy will selectively couple with the higher loss tangent material. Therefore, microwaves can be used for the selective heating of the materials (Thostenson and Chou 1999). This kind of selective heating may lead to some unique microstructures and properties that are not possible to realize in conventional processing methods. Thus the processing of materials by microwave synthesis offer several advantages over conventional heating method, such as energy savings, improved product yield, unique microstructure and properties, lesser processing time, synthesis of new materials and besides this reduction in overall manufacturing cost [Das et al 2009].

1.5 Glass Properties

The properties of glass can be altered by adding other materials such as divalent oxides, heavy metal oxides, rare earth oxides, transition metal oxide etc. For example, a divalent Lead oxide is added for brilliance and weight, boron oxide for thermal and electrical resistance, barium oxide to increase the refractive index in optical glasses, cerium to absorb infrared rays, chromium oxides to impart colour and manganese oxide for decolorizing. If the glass is free from stress and strain, the macroscopic properties of the glass such as optical transmission and absorption, reflection of light, thermal expansion etc are found to be isotropic. Glass is relatively opaque to long - wave infrared radiation and transparent to short - wave infrared radiation. Usually, the infrared transmission is found to vary with the type and
thickness of the glass. The float glasses have tendency to transmit very little in the short wavelength region of the ultraviolet band but the transmission increases as soon as the band of visible light spectrum is approached.

The flexibility of glass composition helps in modifying the properties of glass. Alkali ions can be easily thermally activated and can move from one stable site to another within a glass. Such a movement of alkali ions within a glass structure enables to replace alkali ions near the surface of a glass by other ions of the same valence i.e Na⁺ by K⁺, Na⁺ by Ag⁺ etc. This replacement of alkali ions in the original glass by other ions, partially modifies the composition of the glass and hence its properties. This is particularly important for the modification of electrical, optical and mechanical properties. The structure of a rapidly cooled glass is more open as compared to a slowly cooled one because the freezing-in of the atomic arrangement occurs at a higher temperature. Thus even if chemical composition is same, the properties differ from glass to glass.

1.6 Types of Glasses

Substances which can form non-crystalline solids are usually found in oxide, halide and chalcogenide systems. Oxide glasses have considerable potential advantages over non-oxide materials because non-oxides readily react with water and atmospheric oxygen to form oxides. Depending upon chemical composition, a large number of glasses with different chemical and physical properties can be prepared. Chemical composition is chosen depending upon the required application of the prepared glass. Glasses differ in types according to the addition and variation of ingredients and hence can be classified into different groups according to their chemical composition. On the basis of chemical compositions, glasses can be divided into following categories:-borate glasses, vanadate glass, alkali borate glasses, silicate
glasses, phosphate glasses, manganese glasses, halide glasses, ceramic glasses, metallic glasses and so on. Of these some of the oxide and other types of glasses are discussed in the following sections:

1.6.1 Borate Glasses

Borate glasses can be easily vitrified. Pure B_2O_3 glass is affected rapidly by the atmospheric moisture. Borate is one of the good glass former. B_2O_3 glass usually consists of three coordinated borons, hence the basic structural unit is a BO_3 triangle with B slightly above the plane of three oxygens. But alkali added borate glasses are quite stable and they are technologically important. The Boron atoms coordinate with either three or four oxygen atoms, depending upon alkali content and various structural units present in several borate glasses are as shown in Fig.1.4. The structure of both crystalline and vitreous glassy B_2O_3 consists of planar [BO_3/2]^0 triangles. The B-O-B angle in amorphous B_2O_3 is found to be between 120\(^\circ\) and 130\(^\circ\) with most of the triangles arranged into boroxol rings in which three oxygens are part of the ring and three outside the ring. It can be seen in Fig. 1.4 that boroxol rings are inter connected randomly with loose [BO_3/2]^0 triangles in the glass. The connectivity and network dimensionality are enhanced because of the addition of alkali oxide in the B_2O_3 network which creates [BO_4/2]^- units. Pye et al [1978] and Wong et al 1976 have reported about the conversion of [BO_3/2]^0 to [BO_4/2]^- by alkali oxide. The BO_4 groups are responsible for the compactness and strength of the structure because these groups are bonded to the rest of structure in four directions and the structure is therefore tied together in three dimensions rather than two. Borate glasses are the most extensively studied glasses in the literature due to its peculiar properties [Konijnendijk 1975; Bray 1999].
Series of papers on borate glass structure by Krogh-Moe J [1958, 1962, 1965] contributed on the basic glass structure. Even now all new data and concepts are currently compared with Krogh-Moe’s structural theory of the alkali borate system. Krogh-Moe proposed that borate glasses contain well defined and stable polyborate groupings which also occur in borate crystals. Fig. 1.5 shows some of these groupings.
Youngman and Zwanziger [1994] had reported with the help of boron NMR spectra that the structure for vitreous $\text{B}_2\text{O}_3$ consists of 1:1 ratio of boroxol rings to boron trioxide units. The structures of boron-based glasses can be extensively studied using Infrared spectroscopy, NMR spectroscopy, Raman spectroscopy, simplified structural models, statistical thermodynamic model etc. The study of borate glasses are particularly interesting because of the so-called boron anomaly. The existence of the boron anomaly which is a variation of thermal coefficient with glass composition in sodium borate glasses has served as the basis in the early models for the structure of the alkali borate glasses. Gooding and Turner's [1934] plot on the thermal expansion coefficient of sodium borate glasses as a function of the added alkali shows a marked decrease in expansion coefficient with simultaneous increase in density which is quite evident from Fig.1.6. Biscoe and Warren [1938] reported about decrease in thermal expansion coefficient between 0 to 16 mol % Na$_2$O, as sodium
oxide replaces boric oxide in the glass composition. This was as a result of the
progressive change of boron from a three–fold boron (B$_3$) to four–fold (B$_4$)
coordination and due to formation of non-bridging oxygens (NBOs) as sodium oxide
replaces boric oxide in the glass composition. There was a minimum observed in
thermal expansion coefficient at 16 mol% Na$_2$O because of the increase in B$_4$ which
in turn increases the connectivity and causes a decrease in thermal expansion and
increase in viscosity. As the concentration of alkali is increased beyond 16 mole %
thereafter there is an increase in thermal expansion coefficient and decrease in
viscosity because further addition of alkali oxide causes the production of NBOs and
this extreme behavior was termed the boron anomaly.

![Fig. 1.6. Thermal expansion coefficient and density of Na$_2$O-B$_2$O$_3$ glasses](Image)

[Gooding and Turner 1934].

1.6.2 Silicate glasses

Silicate glasses are of technological importance, since these glasses are not
easily affected by atmospheric moisture, acids etc. Silicate glasses form three-
dimensional network of tetrahedral units $[\text{SiO}_{4/2}]^0$. All the four oxygens in SiO$_4$ tetrahedral are randomly connected to one, two, three or four, depending upon the other oxides present [Rao K.J 2002]. The addition of modifier oxide usually creates non-bridging oxygens by the breakage of Si - O - Si bonds and the modifier cations will remain in the network interstitial position as depicted in Fig. 1.7. When Na$_2$O is added to SiO$_2$, Si - O - Si linkages break to from Si - O terminations as below:

$$\text{Na}_2\text{O} \rightarrow 2\text{Na}^+ + \text{O}^{2-}$$

$$2[\text{SiO}_{4/2}]^0 + \text{O}_2^- \rightarrow 2[\text{SiO}_{3/2}\text{O}]^-$$

$$\text{Na}_2\text{O} + 2[\text{SiO}_{4/2}]^0 \rightarrow 2[\text{SiO}_{3/2}\text{O}]^- + 2\text{Na}^+$$

Fig. 1.7. Creation of non-bridging oxygens (NBOs) in a sodium silicate glass [Jen et al 1980].
1.6.3 **Vanadate glasses**

There are only a few reports on amorphous V$_2$O$_5$ glasses prepared by microwave method in the literature. Due to limited experimental results, the nature of structure and bonding of vanadium in glasses is still incompletely understood. V$_2$O$_5$ is not a good former and the melts of V$_2$O$_5$ tend to crystallize, but amorphization in V$_2$O$_5$ can be achieved by using fast quenching techniques, such as splat cooling or thermal decomposition [Denton *et al* 1954].

![Structural groups of V$_2$O$_5$.](image)

*Fig. 1.8. Structural groups of V$_2$O$_5$.***
Although V$_2$O$_5$ does not form glass by itself, but it readily form glass in polynary combinations with V$_2$O$_5$, TeO$_2$, P$_2$O$_5$, B$_2$O$_3$, SiO$_2$ etc. Among the other complex systems are V$_2$O$_5$ - TeO$_2$, BaO - V$_2$O$_5$ - TeO$_2$, GeO$_2$ – V$_2$O$_5$ and CaO - V$_2$O$_5$ - TeO$_2$, CaO - B$_2$O$_3$ - V$_2$O$_5$ etc. The structure of amorphous V$_2$O$_5$ is complicated because of the capability of vanadium atoms to assume different valence states i.e. V$^{4+}$ and V$^{5+}$. Many vitreous vanadate systems have the properties of semiconductors. The modified structural groups of V$_2$O$_5$ are shown in Fig.1.8. Actually amorphous V$_2$O$_5$ is a semiconductor whose resistivity is an order of magnitude higher than that of crystalline V$_2$O$_5$. Addition of modifier oxide into vanadate glass network leads to the network modifications which plays an important role in the study of conductivity, thermal and spectroscopic properties.

1.6.4 Phosphate glasses

P$_2$O$_5$ containing glasses have several superiorities over archetypal silicates and borate glasses due to their distinctive properties such as high thermal expansion coefficients, low melting temperatures, low softening temperature and high ultra-violet transmission [Ahsan et al 2001; Richard et al 1997]. Besides, poor chemical durability, high hygroscopicity and volatile nature of phosphate glasses have prevented them from finding technological applications. The network of phosphate glasses contains a polymeric structure, where the network is dominated by linkages between PO$_4$ tetrahedra. In the case of vitreous P$_2$O$_5$, these groups are connected to adjacent units by three of their four vertices and one place is occupied by a terminal, double-bonded oxygen atom [Moustafa et al 1998]. However, alkali modified phosphate glasses are highly stable and this can also be achieved by adding heavy metal oxides into P$_2$O$_5$ glass network [Sidek et al 1998]. Because with the addition
of alkali oxide to P\textsubscript{2}O\textsubscript{5} glasses, the phosphorous retains fourfold coordination throughout the full composition range from pure P\textsubscript{2}O\textsubscript{5} to the fully alkali oxide saturated orthophosphate MPO\textsubscript{4} [Martin 1991]. Unlike B\textsubscript{2}O\textsubscript{3} and GeO\textsubscript{2}, phosphorous in P\textsubscript{2}O\textsubscript{5} based glasses retains its four coordination [Van Wazar 1950]. Melts of simple phosphates contain chains and rings in equilibrium while in highly modified glasses, the phosphate chain lengths decreases [Sales \textit{et al} 1984]. Properties of the alkali phosphate glasses are influenced by the distribution of polymeric anions in the network. In view of these, metal oxides such as CaO, MnO\textsubscript{2}, ZnO, Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, etc have been added to sodium phosphate glasses [Sahaya Bhaskaran \textit{et al} 2007]. Phosphate glasses containing transition metal ions have unique properties which led to many technological applications such as electronic and electro-optical devices [Cozar \textit{et al} 2008].

1.6.5 Manganese glasses

Manganese ions have been frequently used as paramagnetic probes to explore the structure and properties of vitreous systems, as their ions have a strong bearing on the optical and magnetic properties of glasses. The study of manganese ion environment in various inorganic glass systems have been reported [Vaidhyanathan \textit{et al} 1994; Sreekanth Chakradhar \textit{et al} 2003; Rami Reddy \textit{et al} 2006], as it exists in different valence states with different co-ordinations in glass matrices. Thus the study is mainly dependent on the quantitative properties of glass formers, modifiers, size of the ions in the glass structure and the field strength etc. Manganese usually exist as Mn\textsuperscript{2+} and Mn\textsuperscript{3+} states in glass, which imparts colour to the glass. The host glasses are found to effect the manganese glasses to a larger extent. Mn\textsuperscript{2+} ions (3d\textsuperscript{5}) produces green emission in silicate glasses and ceramics and are found to possess high optical basicity due to tetrahedral coordination. Mn\textsuperscript{2+} ions when doped with fluoride and
phosphate glasses produces broad orange-red emission and possess low optical basicity due to octahedral coordination. The Mn$^{2+}$ ions impart faint pink colour and Mn$^{3+}$ ions give a deep purple colour to glass and the glasses melted under atmospheric conditions show two states mixed together with the colour of the trivalent manganese prevailing [Bhatnagar 1939]. The observed absorption band due to Mn$^{3+}$ ions is attributed to the spin allowed transition $^5\Gamma_3 \rightarrow ^5\Gamma_5$ [Bamford 1962].

1.6.6 Neodyate glasses

Neodymium is one of the most studied rare-earth ions and is found to have immense applications in photonic devices [Gatterer et al 1998; Pisarski et al 2005 and Maumita Das et al 2006]. Neodymium doped phosphate glasses are widely used in high average power laser solid state lasers, laser material processing, ranger finders and other industrial and scientific applications. The absorption and emission spectra of Nd$^{3+}$ in several crystalline and glassy host lattices have been investigated extensively [Reisfeld et al 1977, 1987] because of this potential laser applications. Nd$^{3+}$ has the $4f$ electronic configuration with $^4I_{9/2}$ ground state. The effective coordination number of Nd$^{3+}$ ion varies from 6 to 9. The transition $^4I_{9/2} \rightarrow ^2P_{1/2}$ of Nd$^{3+}$ in the absorption spectra is characteristic of coordination of the rare earth ion in the crystalline and glassy host matrices. Differences in the coordination leads to a variation in the energy of the above transition from 23,217 to 23,385 cm$^{-1}$ [Yatsimirskii et al 1979]. The Judd-Ofelt theory can be used to evaluate the radiative parameters of Nd$^{3+}$ ion. The parameters that could be obtained from optical absorption spectra of the sample include radiative transition probability, energy transfer probabilities, branching ratios, excited state lifetimes, quantum yield, non-radiative relaxation rate, and laser cross sections [Reisfeld et al 1985]. With the alteration in the chemical composition in the glass, there are significant changes in
spectroscopic parameters and the optical and spectroscopic properties of a laser gain material are used in designing laser device. Doping with Neodymium in the phosphate network can give highly stimulated cross-section. Many Nd$^{3+}$ doped glasses and crystals have been identified as active media for solid state lasers.

1.6.7 Other glasses

1.6.7 (a) Metallic glasses

Besides the glasses discussed above, there are metallic glasses which are alloys having amorphous or glassy structures. Metallic glasses also known as amorphous metal, is usually an alloy rather than a pure metal. These glasses are much tougher and less brittle than oxide glasses and ceramics. These glasses have electrical, optical and magnetic properties like metals. As the electrical resistivity of the metallic glasses doesn’t vary much with temperature, these find immense applications in electronic circuits like magnetic tape recording heads, magnetic sensors or transducers, security systems, motors, power transformer cores and as inductors in magnetic separation equipment. These glasses can be drawn into thin tapes or fibers using very high speed quenching techniques and are used inside thermonuclear reactors because of their less susceptibility to radiation damage. Glasses are usually found in the form of silicate glasses which consists of mostly silica and other oxides of sodium, manganese, aluminium and so on. In order for the glass to possess metallic properties, it should be synthesized from the melts of metallic elements instead of oxides. However, liquid metals and alloys crystallizes rapidly on cooling and thus it was in 1960 that the first true metallic glass was obtained which consisted of an alloy of gold and silicon (Au$_{80}$Si$_{20}$), containing 80 at. % Au and 20 at. % Si [Klement et al 1960]. The glass-forming ability of these glasses depends on various factors like
enthalpy of mixing, atomic size and multicomponent alloying. A number of processes like solidification or solid state processing can be used to synthesize bulk metallic glasses. Bulk metallic glass (BMG) and its composites are found to have unique properties as compared to its crystalline counterparts like mechanical, magnetic and corrosion-resistance and are highly potential for structural and functional applications [Inoue et al 2004 ; Zhang et al 1998, 2003].

1.6.7 (b) Halide Glasses

Halide glasses belong to non-oxide glass category and contain elements of group VII elements (Halogens) of the periodic table namely F, Cl, Br, I as anion instead of oxygen. BeF₂, ZnCl₂ and AlF₃ are the oldest known halide glass formers, but are found to be hygroscopic materials and hence undergo crystallization. ThCl₄, BiCl₃, CdCl₂, CdI₂ and ZnBr₂ glasses are good glass formers but their glass forming ability and chemical durability are not as good as silicate glasses. The low transition temperatures of these glasses limit their practical applications. Heavy metal fluoride glasses such as ZrF₄, HfF₄ and ThF not only act as glass formers, but are found to have better transmission in the IR region. Currently extensive research is going on halide glasses [Moynihan et al 1987].

1.6.7 (c) Chalcohalide Glasses

Chalcogenide glasses which means ‘ore former’ are a group of non-oxide vitreous materials and these glasses contain elements of group VI of the periodic table namely Sulphur, Selenium and Tellurium as glass forming anions instead of oxygen [William B Jensen 1997]. These glasses are obtained by melting group VI elements with one or more group V and IV elements. Compositions modified by adding halogens are called "chalcohalides". These are found to transmit from approximately
1μm to infrared wavelength. The bonding in these glasses are found to be fairly covalent and are found to be good semiconductors with electronic conductivity in the range of $10^{-3}$ to $10^{-13}$ ohm$^{-1}$ cm$^{-1}$. These glasses show semi conducting behavior, photoconductivity and IR transmitting properties and are used as optical elements in the instruments for the infrared region, where they transmit radiation of considerably longer wavelengths than oxide glasses [Bach et al 1995].

1.6.7 (d) Glass-Ceramics

Glass ceramics have properties common to both glasses and ceramics. These can be synthesized through controlled crystallization of base glass as they possess amorphous and one or more crystalline phases. Yao et al [2005] has reported about the synthesis of these polycrystalline materials by controlled crystallization of base glass. It is found to have characters similar to those of ceramics like zero penetrability, opacity, firmness, coloration, low or even negative thermal expansion, high uniform temperature conditions, blazing, machinability and high break down voltage which can be adapted by controlling the base glass composition. Glass ceramics of the type Li$_2$O - Al$_2$O$_3$ - SiO$_2$ system (LAS system) are used as insulators for spark plug because these are found to be good non-conductors with high mechanical strength at high temperatures. MgO - Al$_2$O$_3$ - SiO$_2$ system (MAS system) are known to be wear resistant and are used as building materials. ZnO - Al$_2$O$_3$ - SiO$_2$ system (ZAS system) are found to be resistant to thermal shock and are used as nose cones on rockets and cookware. These properties finds it to have applications in aerospace technology as it can withstand the action of high temperature under corrosive environments. The high temperature resistant coating compositions are based on alkali free barium silicate glass compositions.
All important achievements in the field of glass science had technological motivations. Glass contributes significantly to the world economy. The annual global demand for flat glass is around 3.5 billion square meter worth (US$40 billion). The demand for windshield glass with solar control, antiglare, de-icing, and de-misting properties and greater integration of communication and security electronics is also growing. Silica fibre used for optical communication is a significant part of information technology. Glass used for containers, bulbs, chemical glass-ware and other products constitutes a significant portion of industrial production in all major countries.

Glasses find several technological applications due to its isotropic conduction, absence of grain boundaries, wide range of control of properties with change in compositions, ease of fabrication into complex shapes, wide selection of glass forming systems, resistance to environmental factors etc. A wide range of controllable optical, mechanical, thermal and other properties make the glasses the most useful class of materials in which the form and function can be combined at will. The properties like hardness and transparency at room temperature along with sufficient strength and excellent corrosion resistance, make glasses indispensable for many practical applications. For example, the hardness of glass is a crucial issue in the development of scratch-resistant glass covers for personal electronic devices [Morten et al 2010]. The enhanced conductivity in glasses results due to the creation of structural disorder during the fusion of glasses. Glasses when doped with rare earth ions finds numerous applications in tele-communications. These materials find potential applications in optical fibers, solid electrolytes, electronic displays, high performance composite, biocompatible implants, dental posterior materials, nuclear
waste management etc. The semiconducting glasses can be fabricated easily and are known to have potential applications as solid electrolytes.

In recent times, glass has found specialized uses as heat insulator for energy conservation, safety glasses, contact lenses, optical fibre optics etc. There are efforts to develop bio-glasses to repair bone structure as they have an ability to coexist with living tissue. About 20-30 microns of phosphate glass added with Yttrium-90 are used as radiation dose for cancerous tumors in the liver [Yakhmi 2009]. The “ab initio” single overlap model is used for analysing the correlation between optical properties of the Eu$^{3+}$ steady-state and time resolved site-selective laser spectroscopies.

In the absence of long range order in glasses, determination of glass structure involves the characterization of different kinds of structural units present in them. The aim of this thesis is to examine the physical, thermal, and optical and transport properties of transition and rare earth metal oxide ion containing glass systems prepared by novel microwave method. Studies on the glasses containing dopant oxides such as transition and rare-earth oxides are effective and useful to observe the conducting and optical properties of the glass matrices. The content of such dopant ions in diverse environments with different valence states that exist in the glass depends on the quantitative properties of modifiers and glass formers. Hence, the structural modifications are expected to enhance and widen the potential applications of the glass matrix and the studies are expected to be highly interesting.