Chapter-I

Introduction

In this chapter, the main points relating to the glasses studied here will be outlined. It will begin with a general introduction of glasses, nature and types of glasses. Different structural theories and kinetic theory of glasses are also discussed.

1.1 Introduction:

Amorphous means "structure less" or capable of assuming any structure. Glass is an amorphous solid usually formed by the solidification of a melt without crystallization. Amorphous substances are isotropic, like gases and liquids and are characterized by short range order. All glasses are amorphous, but not all amorphous substances are glasses. Highly disperse powders, such as many precipitation products from aqueous solutions, including certain hydroxides, sulphides and selenides, or intermediate products resulting from certain reactions with solids, as well as thermally unstable gels, can be amorphous, but must not be understood as glasses. Glasses can be recognized by its transparency, hardness, shining, form and often by beautiful colours. Many household objects are made of glass such as light bulbs, mirrors, aquaria, cathode ray tubes, computer flat panel displays, windows etc. In research laboratories, flasks, test tubes, and other laboratory equipments are often made of borosilicate glass for its low coefficient of thermal expansion, giving greater resistance to thermal shock and greater accuracy in measurements.

American Society of Testing Materials (ASTM) [1] defines glass as *"An inorganic product of melting solidified mainly without crystallization."* The amorphous substances, irrespective of the method of preparation, ought to be defined as vitreous if they have a transition temperature region, the property typical of glasses. According to Jones [2], *"glass is a material formed by cooling from the normal liquid state, which has no discontinuous change at any temperature, but has become more or less rigid through a progressive increase in its viscosity"*.

Glasses have numerous properties in common with crystalline solids, such as hardness and elasticity of shape. The problem in preparing a glass from the melt is to maintain the homogeneous and isotropic state of the melt even during cooling, which means that nucleation and crystal growth must be suppressed. The formation of glass from the melt thus requires conditions by which the kinetics of nucleation and crystal growth processes can be made inefficient.

1.2 Characteristic of Glasses:

Compared with crystals, the structure of glass is devoid of regular arrangement of atoms in a periodic lattice. Glasses do not confirm the rules of stoichiometry and exhibit a characteristic thermal event known as glass transition. Glass is the result of a phase transformation in which nucleation and growth of crystals has been suppressed i.e., the time allowed for crystallization has been less than the time required by the kinetic factors of atomic rearrangement. These kinetic factors are temperature dependent and devitrifaction temperature is loosely defined as the temperature below which the crystallization time becomes practically infinite. If a glass is formed by cooling of a liquid or vapor, a fast quench is sometimes required to minimize the time at which the glass is below the melting point but above the devitrifiction temperature [3, 4]. The relation between crystal, liquid and glass can be explained by means of a volume-temperature diagram as shown in Fig.1.1. The structure of solid formed by cooling from its liquid state depends on many factors; one important factor is its rate of cooling. If the liquid is cooled from its original state represented by "*a*" in Fig.1.1, its volume decreases steadily. If the cooling rate is low then a discontinuous change occurs at point "*b*" and

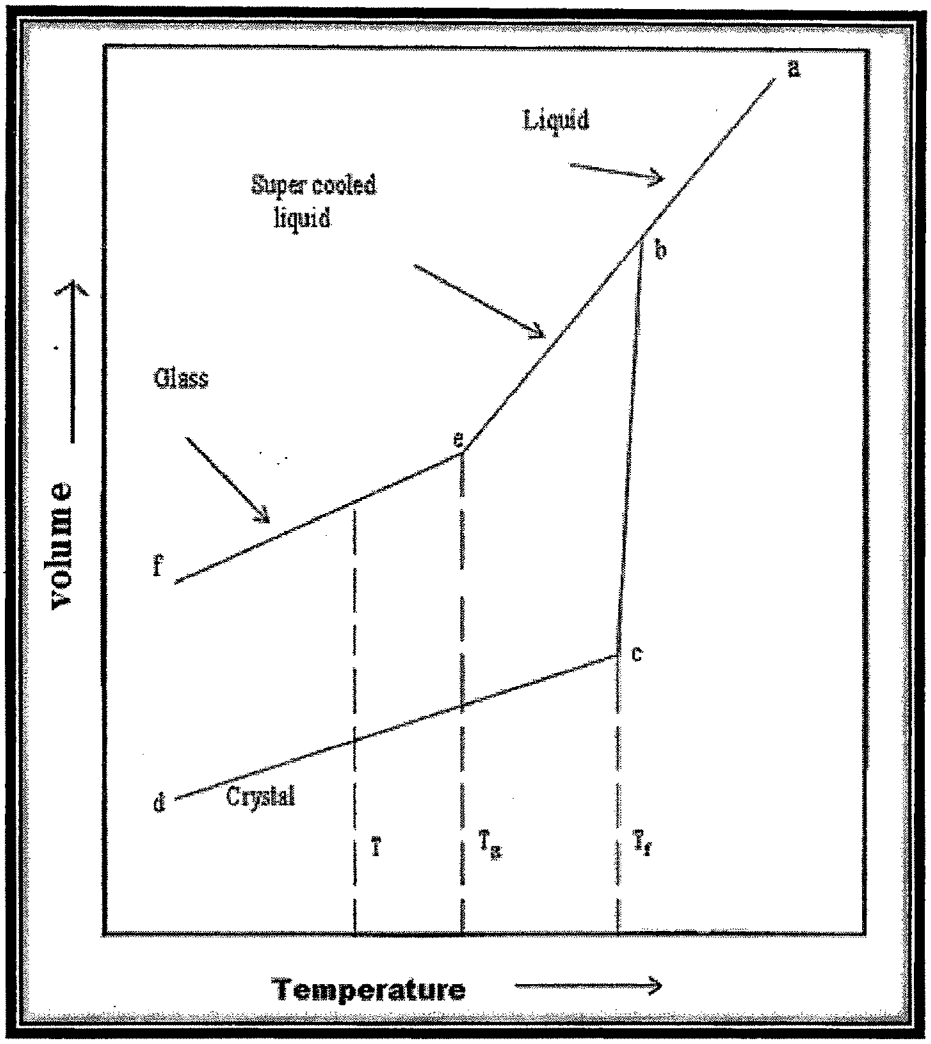


Fig.1.1. Variation in volume with temperature for a glassy and crystalline solid.

follows the path '*bc*', which corresponds to crystallization taking place in the melt. This denotes the *transformation temperature* (T_f). As the temperature is lowered further, the volume decreases but with a slope different from that obtained prior to crystallization. If the cooling rate is very fast, crystallization does not take place at temperature T_f and the volume decreases steadily along line "*b*" up to point "*e*". This point denotes the *glass transition temperature* (T_g), below which the volume-temperature curve undergoes a sharp change. Between T_g and T_f, material is *super cooled* and below T_g, the rearrangement of atoms and molecules becomes slow and the structure gets frozen and it behaves like a *"solid"*.

Thus, in x-ray diffraction spectrum resultant solid shows, instead of sharp rings, a few diffused halos and possesses a short range order only; i.e., periodicity is maintained only up to a few angstroms and not to large distances. Such a solid is called *"glass"*. Since the volume of the material in the glassy state is larger than that in the crystalline state for a particular temperature (lines "*ef*" and "*cd*" in Figure. 1.1), it is obvious that thermodynamically glassy state is a metastable one [2]. Melting is not the only way of producing glasses. There are various techniques, for e.g., condensation of vapours, conversion of crystals to an amorphous form using mechanical means or irradiation with fast neutrons, dehydration and sintering of gels, ball milling etc. The last of the techniques mentioned, has recently gained considerable attention and based on mixing solutions of salts with SiO_2 sol, converting it to a gel, its subsequent dehydration, and finally heating to 600-1000^{0}C. These techniques, which have so far found only limited and special applications, have been surveyed for e.g., by Mackenzie [5], the sol-gel methods by Dislich [6], McCarthy and Roy [7] and Yoldas [8].

1.3 Types of Glasses:

1.3.1 Metallic Glasses:

Some of the metal alloys which can be produced in amorphous form by very rapid cooling (splat quenching technique) are known as *metallic glasses*. These glasses have good corrosion resistance and the absence of grain boundaries. Metallic glasses have high electrical and thermal conductivity, have metallic luster and are not ductile and strong. The metallic glasses can be used in magnetic sensor or transducers, security systems, motors and power transformer cores and can be used as inductors in magnetic separation equipment. The first true metallic glass, $Au_{80}Si_{20}$, an alloy containing 80 atomic % Au and 20 atomic % Si was obtained in 1960. Thereafter a number of metallic glasses were invented such as $Al_{90}Ni_6Nd_4$ [9], Co-Nb-B-Cu [10], Al-Fe-Nb [11], Fe-P [12], Fe-Ni [13] etc.

1.3.2 Halide Glasses:

Halide glasses have been considered to have the most appropriate optical properties for ultra-low fibers because of their wide transmission wavelength range. Elements of halide group (F, Cl, Br, I) also form glasses with other V, VII groups of elements, e.g., B_2O_3-SiO_2-CuO-NaX (X= Cl, Br) [14], AgX (X= Cl, Br, I) [15], alkali-fluoride-beryllium, Li-F glasses, iodine glasses etc. Out of which iodine glasses have good far IR transmission and moisture resistance properties [16].

1.3.3 Chalcogenide Glasses:

These glasses are derived from chalcogeneous elements S, Se and Te. They are used as optical elements in instruments for the infrared region, where they transmit radiation of considerably longer wavelengths than oxide or fluoride glasses. However, they show very strong absorption in the visible region. These glasses behave as semiconductors and have been found to exhibit the switching effect. Different chalcogenide glasses have been studied such as As-S-Tl [17], As-Se-Tl [18], Ge-Se-Tl [19], Fe-Se-Pb [20], As_xS_{100-x} [21], $Al_xAs_{40-x}Te_{60}$ [22], Cu-As-Te [23] etc. The mechanical strength and thermal stability of such glasses are much lower than those of oxide glasses and the thermal expansion, temperature coefficient of the refractive index and relative photoelastic coefficient are much higher. Their transparency to IR radiation generally increases towards smaller wave numbers owing to higher atomic masses and smaller bonding force constants [24, 25]. A very high conductivity of the chalcogenide glasses, analogous to that in fast ion conducting oxide glasses, exists in some Li-based chalcogenide systems [26, 27].

1.3.4 Spin Glasses:

These glasses contain interacting atomic magnetic moments and possess some disorderness in their spin, in which the temperature variation of the magnetic susceptibility undergoes an abrupt change in slope at a temperature, referred as (T_f) *freezing temperature*. The spins have no long range magnetic order below (T_g) *glass transition temperature*, but found to have static or quasistatic orientation which varies randomly over macroscopic distances. Large number of spin glasses such as cobalt and manganese-alumino-silicate, $Eu_xSr_{1-x}S$, $Cu\text{-}Ga_x\text{-}Al_x\text{-}Fe_{2-2x}O_4$ [28], Tb_2TiO_7 [29], $KCo[Fe(CN)_6$ [30] etc. have been studied by different workers.

1.4 Inorganic Oxide Glasses:

Inorganic oxide glasses are the oldest known non-crystalline materials. These glasses are of technological importance due to their structural versatility and wide applications. A variety of industrial glasses for packaging, house hold uses, building and construction, electrical engineering and optical applications are manufactured in large industrial plants by the processing of melts, mainly in the open air. Presently, the glasses of any strength one wishes to have between metal and honey, of any conductivity between that of metals and insulators, of any magnetic characteristics between that of air and ferrites and of uses right from detector of nuclear radiation to the source of powerful laser beam have been successfully developed by the suitable material preparation techniques.

The interatomic forces in glasses must essentially be the same as in crystals, since the strength of glass is of the same order as that of crystals. Hence, as in crystals, the arrangement of atoms in glass, which form an extended three dimensional network, is not a periodic one, i.e., glasses exhibit complete absence of long range order but possesses only short range order. This order extends upto 10 to 20 Å [31].

1.5 Structural theories of glass formation:

Glass formation is a kinetic phenomenon; any liquid, in principle, can be transformed into glass if cooled sufficiently quickly and brought below the transformation range. A good glass forming material is then one for which the rate of crystallization is very slow in relation to the rate of cooling. Various theories have been proposed to discuss, how the arrangement of atoms in space and the nature of the bonds between the atoms are related to glass formation, known as the *structural theories of glass formation.*

1.5.1 Goldschmidt's radius ratio criterion:

The earliest effort in understanding glass formation criteria was the structural effort made by Goldschmidt [32]. He derived empirical rules for glass formation. He ascribed the relative size of the cations to be the determining factor for glass formation. His general observation was that, for a simple oxide of formula M_mO_n (M —> cation), the glass formation is only possible when the ratio of atomic radii, r_a/r_c (where '*c*' denotes cation, and '*a*' anion), falls between 0.2 to 0.4.This condition is met for oxides SiO_2, B_2O_3 and P_2O_5 etc. Later, it has been pointed out that even though the ionic radius of BeO allows the formation of the tetrahedron arrangement of oxygen around beryllium ion, BeO cannot be obtained in the glassy state. Hence, this led to develop the random network theory for glass structure.

1.5.2 Zachariasen-Warren random network theory:

The network hypothesis proposed by Zachariasen [33] and reinforced by Warren's [34] x-ray diffraction represented a leap forward in the knowledge about the structure of glasses. Zachariasen did not agree with the crystallite theory proposed by Randall et. al. [35] as assumptions in the theory led to discrepancies between observed and calculated densities of silica glass. Diffraction patterns and thermal properties observed were also not in accordance [33]. These assumptions were: (i) the average linear dimensions of the cristobalite crystallites were of the order of 15Å, and (ii) lattice constants of the crystallites are 6.6% larger than in cristobalite crystals.

Over large temperature ranges, the mechanical properties of glasses are comparable (superior in some cases) to those of crystalline materials. Because of this, Zachariasen proposed that the forces in glasses are essentially the same as those in a crystal, with atoms oscillating about definite equilibrium positions forming an extended three dimensional network [33]. X-ray diffraction data had shown this network was not periodic and symmetrical, but not entirely random, as inter-nuclear distances do not fall below a minimum value. Therefore, all inter-nuclear distances are not equally probable which results in the diffraction patterns seen.

It can be said that the glass network is characterized by an infinitely large unit cell containing an infinite number of atoms. Due to the lack of periodicity, no two atoms are structurally equivalent. The isotropic nature of glass is a direct consequence of this lack of symmetry, as the atomic arrangement is statistically equivalent in all dimensions. As all atoms are not structurally equivalent, the energy needed to detach an atom from the network will be different for each atom. This means with increasing temperature, an increasing number of detached atoms would be expected, so the network breaks down continuously, as opposed to a crystalline material where the breakdown is an abrupt phenomenon. As a result of this, the transition from super cooled liquid to glass occurs over a range of temperatures.

According to the Zachariasen-Warren network theory, the following rules are valid for the formation of low-order 3-D networks i.e., the glass formation of simple compounds such as SiO_2, B_2O_3, P_2O_5 etc.

- An oxide or compound will tend to form a glass if it easily forms polyhedral units as the smallest structural units.

- Polyhedra should not share more than one corner.
- Anions (O^{2-}, S^{2-}, F^-) should not link more than two central cations of the polyhedra.
- The number of corners of the polyhedra must be less than six.
- At least three corners of the polyhedra must link with other polyhedra.

If large cations are introduced into such simple glasses-by melting SiO_2 and Na_2O or CaO, bridges are broken. The oxygen (or other anion e.g., S^{-2}, F^-) with the large cation will assume the site at the free end of the separated tetrahedron, while the large cation itself is accommodated in the large cavity originating in the severance of the network at the site. Cations in the glass were categorized by Zachariasen according to their role in the glass network.

- Network-formers: Si^{4+}, B^{3+}, P^{5+}, V^{+4}/V^{+5},Ge^{4+}, As^{3+}, Be^{2+}, with Coordination Number (CN) of 3 or 4.
- Network-modifiers: Na^+, K^+, Ca^{2+}, Ba^{2+}, Li^+, Ag^+ with Coordination Number (CN) $\geq$ 6.
- Intermediates e.g., Fe, Al, Zr, Ti, Mn, Be, Mg, which may reinforce (CN = 4) or loosen the network further (CN 6 to 8).

The structural implications of this random network model led to the classification of oxides to network formers capable of forming glasses by themselves (for e.g., SiO_2, B_2O_3, P_2O_5, TeO_2, V_2O_5 etc.) and network modifiers (for e.g., CaO, BaO, Na_2O, Ag_2O, K_2O etc.). The latter do not form glass by themselves and only modify the glass structure because of their large ionic radii. They restrict the mobility of the elements which constitute the arrangement during the time of

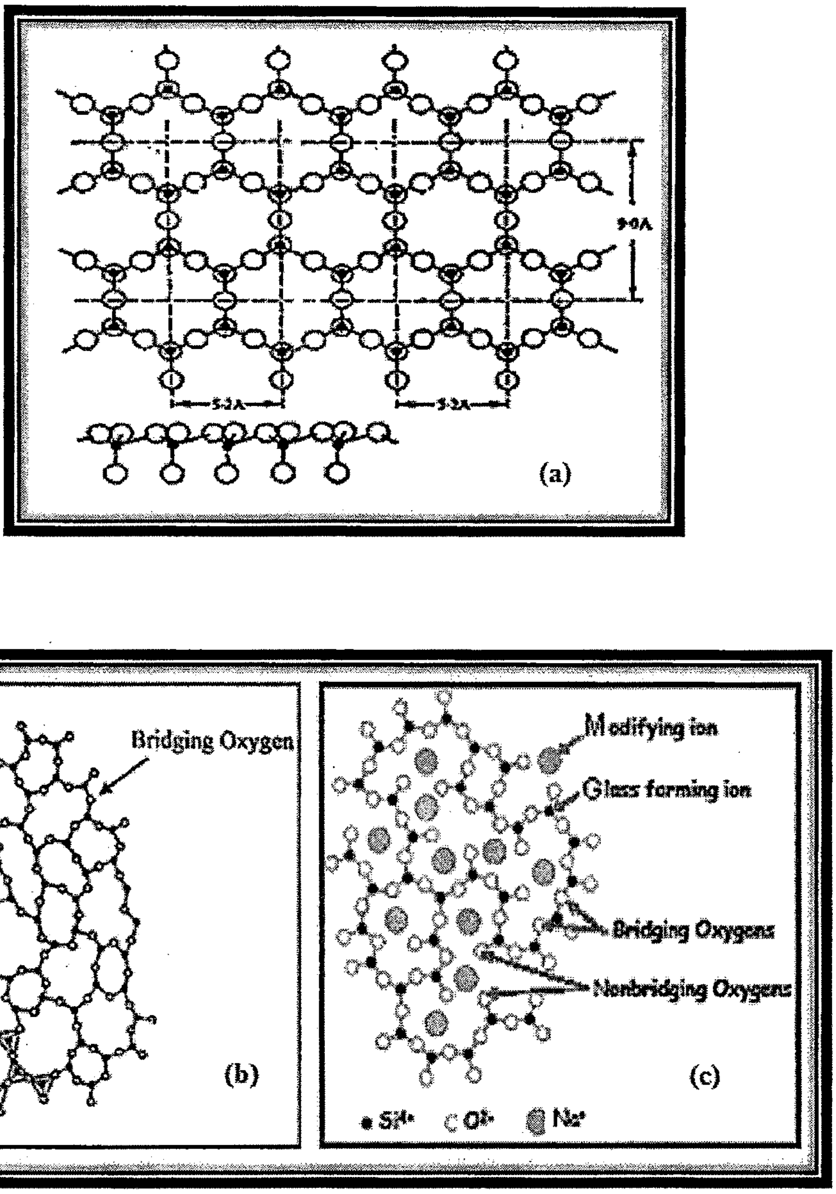
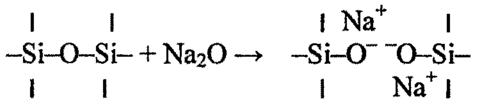


Fig.1.12. (a) Regular periodic arrangement of atoms (or ions) in silicate (SiO_2), (b) Disordered netting of SiO_4 building blocks in SiO_2 glass and (c) Arrangement of atoms or ions in sodium silicate glass. When Na_2O is incorporated, the large sodium ions rupture the oxygen bridges and open (modify) the structure.

cooling. It also produces the non-bridging oxygen's (NBO's) as shown in Fig.1.12 (b). These oxygen atoms are connected with chains from one side and other bond remains free having more negative charge on it, where as bridging oxygen is connected with the anions in the chains from two sides and makes bridge. The material when cooled quickly enough to suppress nucleation and growth of crystals forms glassy state and has an x-ray short range order. Introduction of network modifier disrupts the bonds (e.g., for SiO_2 glass) as



$$\underset{|}{\overset{|}{-\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}- + \mathrm{Na_2O} \rightarrow \underset{|}{\overset{|}{-\mathrm{Si}}}-\overset{\mathrm{Na}^+}{\mathrm{O}^-}\ \underset{\mathrm{Na}^+}{{}^-\mathrm{O}}-\underset{|}{\overset{|}{\mathrm{Si}}}-$$

Figure 1.12 shows the difference between a regular crystalline lattice and random network of an oxide, SiO_2, where the structural units can be tetrahedral. The nature of bonding between cation and oxygen also plays dominant role. Those oxides that have strong covalent bonds are more likely to act as network former than those in which bonding is predominantly ionic.

The Zachariasen random network theory can be used to explain many properties of conventional glasses, such as viscosity-temperature behavior, and electrical conductivity. However, it cannot explain all phenomena, such as property effects thought to be due to short range ordering, and the glass formation in some novel systems also contradict the criteria of this theory.

Besides the above continuously random three dimensional network (CRN) model, other alternate models have also been advocated in which there are regions of order alternating with connecting regions of disorder. These crystalline models, where very small crystalline regions are connected by disorder material, are known as 'micro crystalline' models. Doremus [36], after reviewing various x-ray diffraction studies, had given the conclusion in support of CRN model. However, distribution of metal ions in these glasses is uncertain. Some studies [37, 38] have given the possibility of non-uniform distribution of metal ions and of their 'clustering' in the network. The kinetic theory of glass formation provides a more satisfactory explanation of glass formation of known systems, but the structural theories are still valid and widely used.

1.6 Kinetic approach to glass formation:

Glass formation has been shown in materials of a wide variety of compositional, bonding and structural types. Therefore, considering how rapidly a vapour or liquid must be cooled to avoid a detectable volume fraction of crystallization (e.g., 10^{-6}) can be a useful way of characterizing its glass forming ability. If nucleation frequencies, I (in s^{-1}) and growth rates, u (in cm s^{-1}) are known as functions of temperature, Eq.1.1 can be used to plot a *time temperature-transformation* (TTT) diagram.

$$10^{-6} = \frac{\pi}{3} I u^3 t^4 \qquad \text{.................} (1.1)$$

where, It is the frequency of nucleation with time and u^3t^3 is the growth in three dimensions in time t. Both nucleation frequency I and rate of advance u are inversely proportional to the viscosity of the liquid. Thus a plot is obtained, called a TTT (*time-temperature-transformation*) curve. From the measured TTT plot, it is possible to obtain the time at each temperature before a significant fraction of the under cooled melt has devitrified. This plot has a 'nose' shape with the temperature at the apex of the nose shape arises, as the tendency for

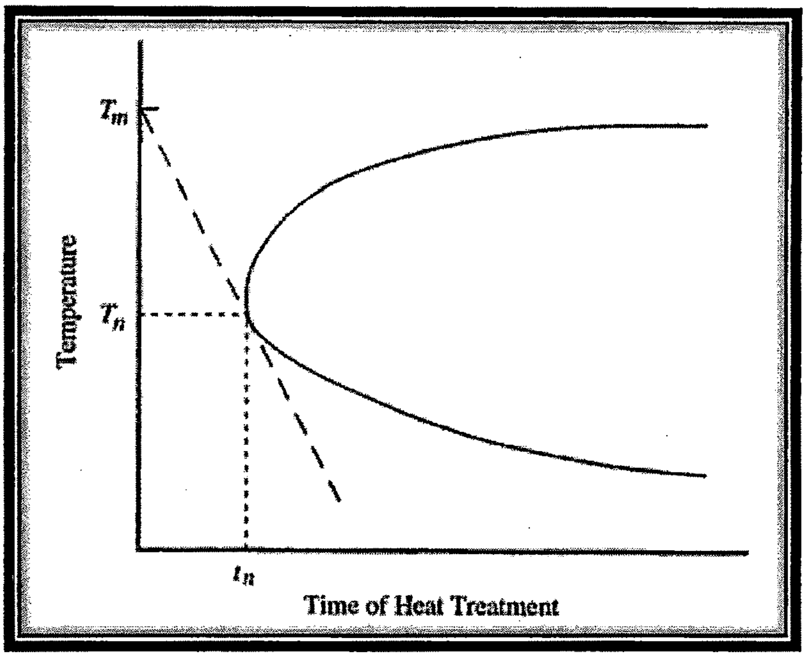


Fig.1.13. A time-temperature transformation curve for a glass forming melt.

crystallization will be initially enhanced thermodynamically on melt cooling, reaching its peak at the apex of the nose. Below this temperature, crystallization is suppressed due to the rising viscosity of the super cooled liquid. The critical cooling rate, $\left[\frac{dT}{dt}\right]_C$ to avoid volume crystallization can be approximately obtained from the TTT diagram (Fig.1.13), at any temperature on the nose, T_n and corresponding time, t_n.

$$\left[\frac{dT}{dt}\right]_C \approx \frac{(Tm-T_n)}{t_n} = \frac{\Delta T_n}{t_n} \qquad \text{....................} (1.2)$$

where T_m is the liquidus (or melting) temperature and T_n is the nose temperature.

1.7 Structure:

1.7.1 Vanadium Structure:

Vanadium oxide is the chemical compound with the formula V_2O_5, commonly known as vanadium pentoxide. Unlike most metal oxides, it dissolves slightly in water due to hydrolysis. Vanadium pentoxide indicates that vanadium is in the +5 oxidation state. The oxygen atoms in the compound are in the -2 oxidation state. Vanadium oxides are important in many respects, because they exhibit useful metal-insulator or semiconductor metal transition as a function of temperature and pressure.

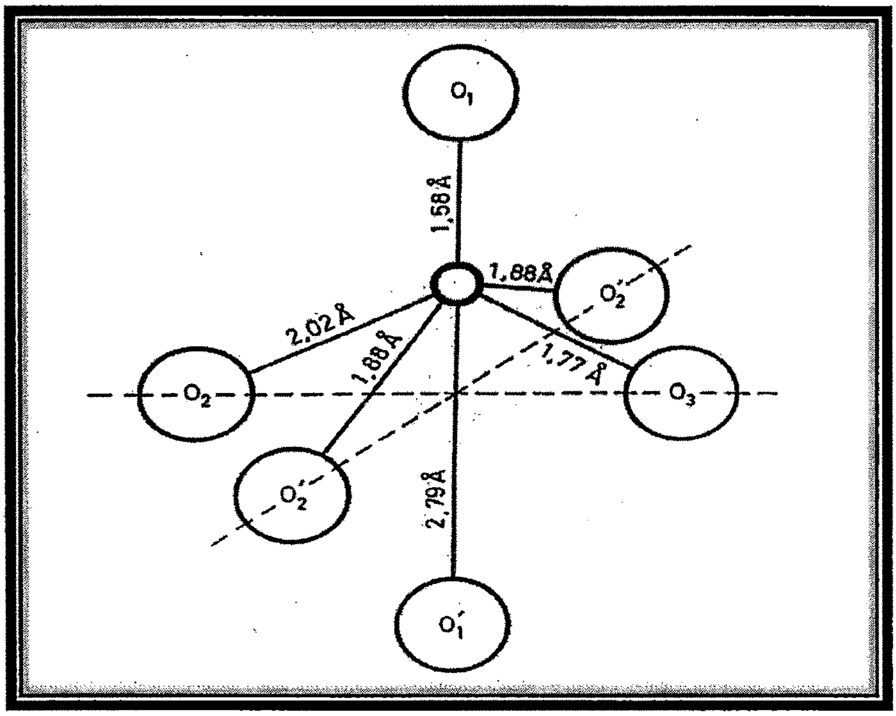


Fig.1.14 (a). Building block of the V_2O_5 structure showing the different V-O distances in the deformed octahedron.

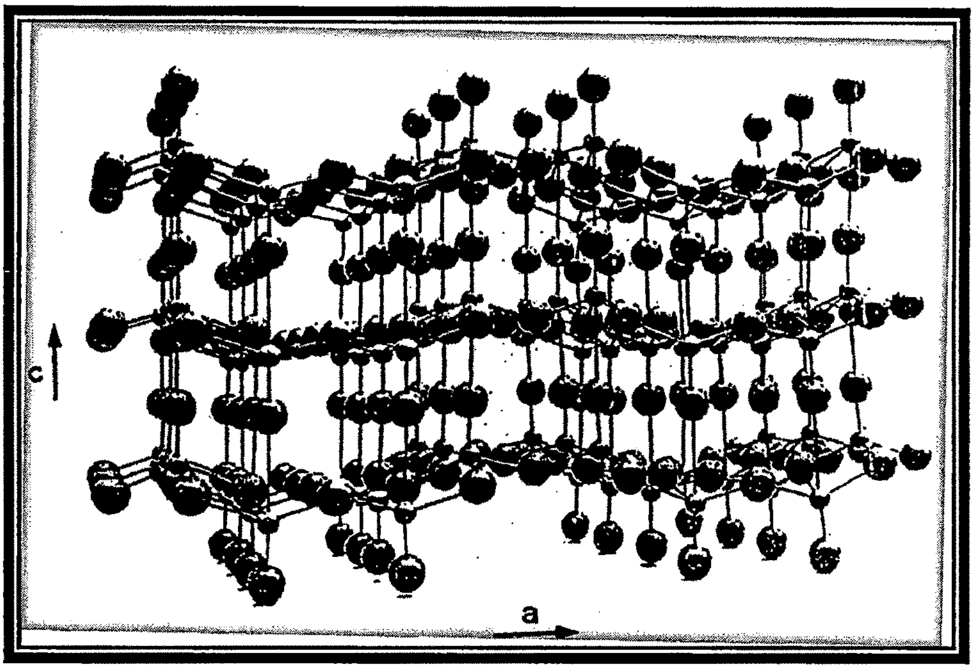


Fig.1.14 (b). Model of the V_2O_5 structure, the a- direction being in the plane of the figure. The large spheres represent oxygen ions, the smaller ones vanadium ions.

The V_2O_5 structure has been determined by Bachmann, Ahmed and Barnes [39]. V_2O_5 has an orthorhombic structure with lattice parameters; a= 11.510 Å, b=3.563 Å and c= 4.369 Å. The building block for this structure is a deformed octahedron (Fig 1.14 (a)), wherein the shortest distance corresponds to a double vanadyl-bond (VO_1=1.585 Å). The V-O distance (V-O_1=2.785 Å) is a weak Vander walls bond. V_2O_5 consequently has a layer structure with an easy cleavage plane the c-plane (Figs. 1.14 (b), 1.15 [(a) and (b)]). The other V-O distances are shown in Fig. 1.14 (a). Vanadium containing glasses exhibits semiconducting properties due to the presence of vanadium in two different valence states i.e., V^{+4} and V^{+5}.

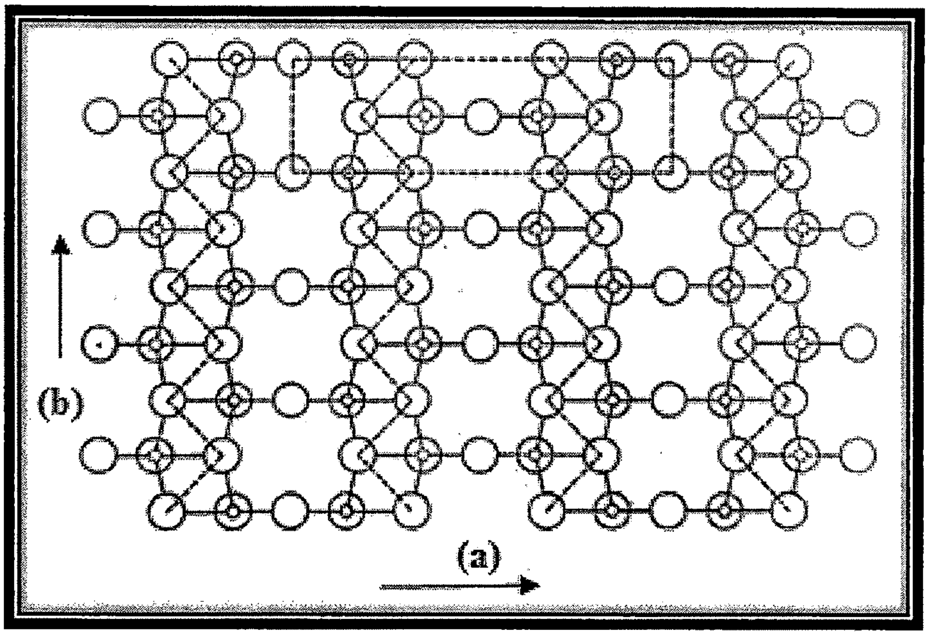


Fig.1.15(a). Projection of the V_2O_5 structure on the c-plane. The rectangular unit mesh in this plane is also indicated.

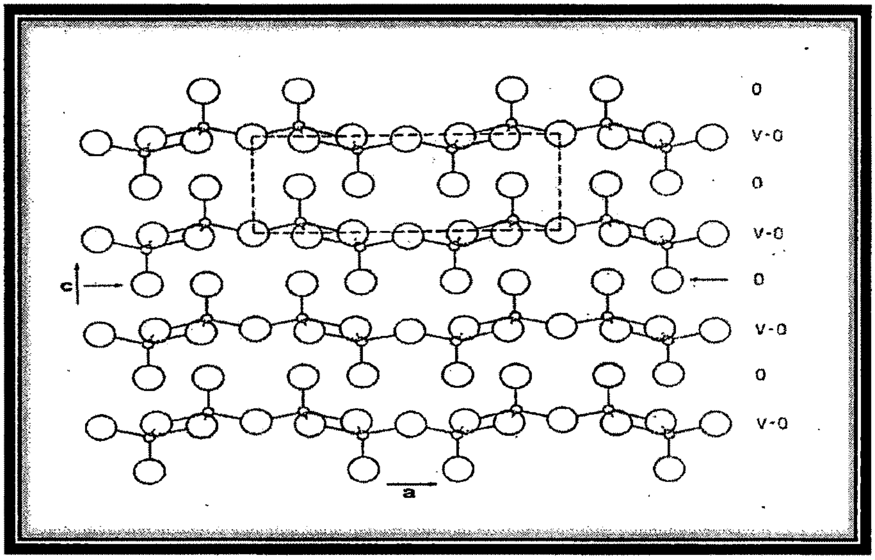


Fig.1.15(b). Projection of the V_2O_5 structure on the b-plane.

1.7.2 Tellurium Structure:

Tellurium is a chemical element that has the symbol 'Te' and atomic number 52. TeO_2 is a solid oxide of tellurium. TeO_2 is highly insoluble in water and completely soluble in concentrated sulfuric acid. Tellurium dioxide is also a conditional glass former, which means it will form a glass with the addition of a second compound such as an oxide or halide in small molar %. Berzelius [40] recognized that TeO_2 can form a glass with various metal oxides, particularly BaO. Later, Lehners et. al. [41] observed glass formation in parts of the systems Na_2O-TeO_2 and K_2O-TeO_2. Structure of TeO_2 is shown in Fig.1.16. In crystalline TeO_2, there are four coordination of Te, with the nearest neighbors being arranged at four of the vertices of a trigonal bipyramids (tbp) and the fifth position occupied by a lone pair of electrons [42].

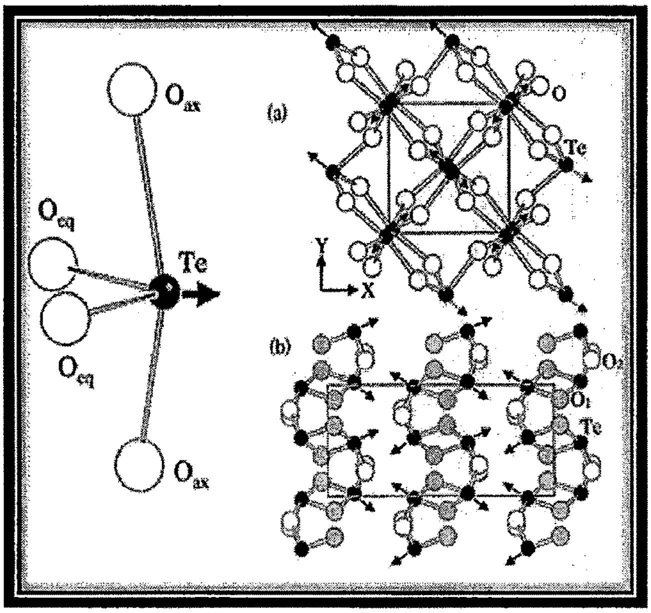


Fig.1.16. Structure of TeO_2: (a) α-TeO_2, and (b) β-TeO_2 (arrows represent the Te 5s electron lone-pair)

The structure of tellurite (β TeO_2) was found to consists of an interconnected network of $(Te_2O_6)^{-4}$ units [43]. The $(Te_2O_6)^{-4}$ unit can be thought of as two trigonal bipyramids, each with an equatorial lone pair of electrons, the bipyramids share an edge. One of the axial Te-O bonds of the bipyramid is slightly longer (2.19 Å) than the other three (average 1.96 Å). The para-tellurite (α-TeO_2), consists of a network of individual interconnected TeO_4 trigonal bipyramids with equatorial and axial bond lengths equal to 1.90 and 2.08 Å, respectively [44].

1.8 Present Investigation:

The electrical properties of semiconducting oxide glasses containing transition metal oxides such as V_2O_5-P_2O_5, V_2O_5-TeO_2,V_2O_5-PbO-GeO_2, TiO_2-V_2O_5-P_2O_5, V_2O_5-B_2O_3 have been reported by several researchers in the past [45- 49]. The electrical conduction in these vanadium based glasses occurs by electron hopping from an ion of the low valence state (V^{+4}) transition metal to an ion of the high valence state (V^{+5}). The oxide glasses, formed with TeO_2 as a network former, possess many interesting properties such as low melting point, high chemical durability, high refractive index and good IR transmitivity, which make them attractive not only from the fundamental point of view but also for practical applications [50, 51]. S. Szu and Chang [52] have suggested that Ba ions, when added in the glass network, progressively block the electronic path and cause a decrease in electronic conductivity. It will create non-bridging oxygen (NBO) and break the glass network. Ag_2O, when substituted in this barium vanadate tellurium oxide glass system, exhibits ionic conductivity. It is observed that the ionic conductivity of oxide glasses always increases with the increase in the alkali ion content in the composition. Silver, Sodium and Lithium glasses based on glass forming oxides such as V_2O_5, P_2O_5 and TeO_2 exhibit high ionic conductivity due to the transport of Li^+, Na^+ or Ag^+ ions [53-57]. Thus, in the present glass system, Ag^+ ions act as charge carriers in this glass system and electronic conductivity is exhibited due to the presence of vanadate oxides. Most published data on mixed electronic-ionic conduction in glasses have been interpreted in terms of an ion-polaron correlation effect [58, 59, 60] which results from the coulombic attraction between oppositely charged carriers.

In the present work, a systematic study on Silver based Barium Vanado-Tellurite glass system is made using different techniques. Preparation of above glass system with splat quenching technique has been attempted to understand the effect of the variation of modifier. Characterization of the glasses using X-ray diffraction, thermal studies by Differential Scanning Calorimetry (DSC), variation in molecular structural units by Fourier Transform Infrared Spectroscopy (FTIR), density measurements by Archimedes principle and transport number measurement by EMF method have been attempted. Electrical conductivity as a function of temperature and composition in the form of complex impedance, dielectric and modulus has also been carried out.

The following three series of glass systems have been prepared and discussed in the present thesis.

1) $x\,(BaO : 1.5\,Ag_2O) - (95-x)\,V_2O_5 - 5\,TeO_2$;

   where $x = 25, 30, 35, 40, 45$.

2) $10\,BaO\text{-}y\,Ag_2O\text{-}(85-y)\,V_2O_5\text{-}5\,TeO_2$;

   where $y = 20, 25, 30, 35, 40, 45, 50, 55$.

3) $5\,BaO\text{-}z\,Ag_2O\text{-}35\,V_2O_5\text{-}(60-z)\,TeO_2$;

   where $z = 25, 30, 35, 40, 45, 50, 55, 60$.

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