CHAPTER 1

Introduction

CHAPTER: 1

INTRODUCTION

1.1 INTRODUCTION:

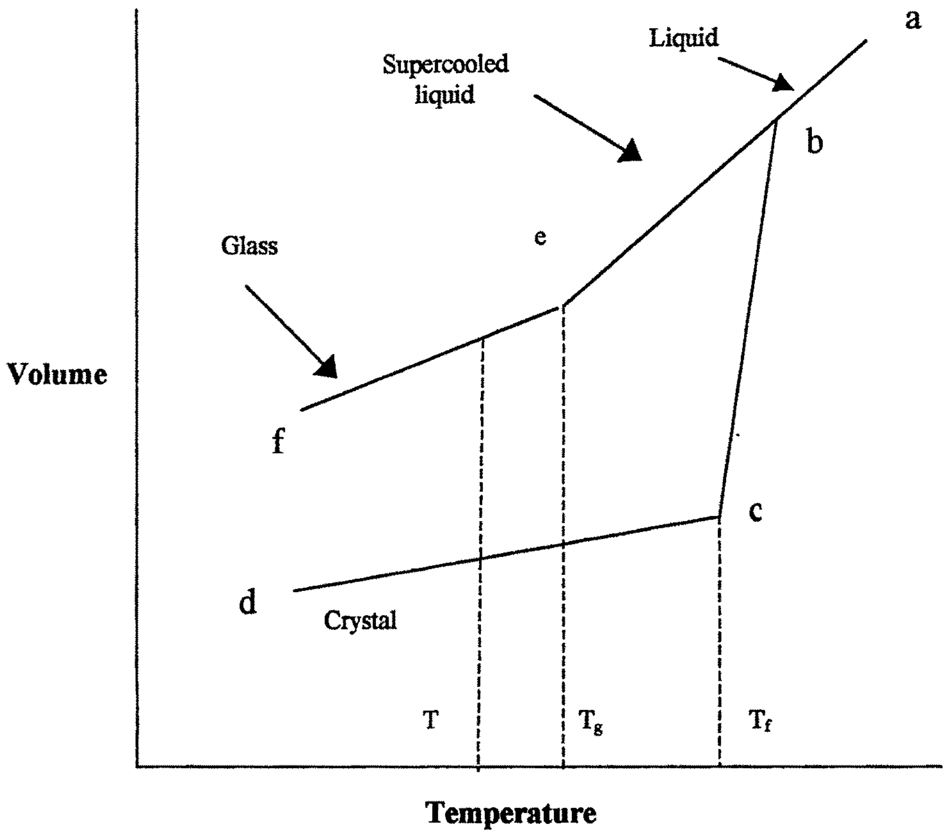
Since the beginning of human civilization, glass has been considered to be one of the oldest man made material. The glasses were first made by man about 4000 years ago in ancient Egypt. Initially, used as an aesthetic appeal, glass has slowly encroached into our daily life in a variety of forms with the passage of time.

Glass can be recognised by its transparency, hardness, shining, form and often by beautiful colours. For a long time, glass remained to household, potteries, lens, windows etc. and no technological uses were explored. After 1800, various compositions were studied to use them as optical glass. Scientific & technological progress continued, when borosilicate glass composition was developed and later, glass of various refractive index, thermally and chemically resistant, photoresistive, photochromatic glasses were developed. Other glasses like laminated glass, glass for vehicles and bullet proof purposes, optical glass fibres, semiconducting glasses, glass ceramics for missile cones and glass lasers to generate power as high as few terrawatts were investigated. Some of the other important applications in the field of optics are the use of laser range finder, infrared transmission glasses for night vision, special glass coatings for selective transmission or reflection of light and remote sensing through optical fibres. In the field of composites, glass fibre reinforced plastics (FRP) are already having thousand of applications. Glass fibre reinforced gypsum (GRG) can be used as a substitute of wood while glass fibre reinforced cement possess sufficient strength and toughness for various constructional applications replacing conventional reinforced concrete.

1.11. GLASSES:

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 at sufficiently slow rate the transformation of liquid into solid is discontinuous as evident by the sharp change in volume at a particular temperature called *"transformation temperature (T$_f$) "*. The solid thus obtained has its atoms or molecules stacked in a regular manner with the periodicity extending over large distance as compared to the atomic dimensions and is said to exist in "crystalline state". X-ray diffraction patterns show sharp rings. However, if the liquid is cooled fast enough, the transformation to solid state is continuous and the volume temperature curve which is a straight line undergoes a change in slope at a particular temperature, T_g, usually referred to as *"glass transition temperature (T_g) "*, Figure 1.11. The substance possess liquid like properties above this temperature and has a value of viscosity about 10^{13} poise at T_g. Below T_g, the rearrangement of atoms and molecules become slow and the structure gets frozen and it behaves like a solid. Thus resultant solid shows, instead of sharp rings, a few diffused halos and possesses short range order only, i.e. periodicity is maintained only up to a few angstrom and not to large distances. Such a solid is called *"glass"*.

The National Research Council Ad Hoc Committee on infrared transmission materials[1] suggests that a glass is an X-ray amorphous solid which exhibits the glass transition. Whereas according to Morey[2], *"glass is an inorganic substance in a condition which is continuous with, and analogous to, the liquid state of the substance but which as a result of having been cooled from fused condition, has attained so high a degree of viscosity as to be for all practical purposes rigid. "*



T_g : Glass Transition Temperature T_f : Transformation Temperature

Figure 1.11 Relation between glassy, liquid and solid

According to Jones [3], a definition of glass is *"a material formed by cooling from the normal liquid state, which has shown no discontinuous change at any temperature, but has become more or less rigid through a progressive increase in its viscosity"*. Glasses can also be prepared without cooling from the liquid state, e.g., glass coatings are deposited from the vapour and sometimes with chemical reactions.

The word ***'glass'*** comes from Indo-European root meaning ***'shiny'*** and vitreous in Latin word for glass. According to applications of the glasses for scientific and technological purposes, various types of glasses such as inorganic oxides, chalcogenide, halide glasses, metallic, spin glasses etc have been investigated. Few of the glasses of academic interest are discussed below.

Chalcogenide Glasses :

Chalcogenide glasses are defined as non-crystalline solids solidified from melts of the chalcogens S, Se and Te and their combinations with elements of groups IV, V, VII including addition of many other elements like As, Ge, P etc. The cation: anion ratios,. however, in chalcogenide glasses can be varied with very large limits since excess S, Se or Te remain liquid in their melting ranges. To avoid easily occurring oxidation of chalcogens, chalcogenide glasses must be melted under an inert atmosphere, usually sealed in vacuum in containers. Different chalcogenide glasses had been studied such as As-S-Tl[4], As-Se-Tl[5], Ge-Se-Tl[6], Fe-Se-Pb[7], As_xS_{100-x}[8], $Al_xAs_{40-x}Te_{60}$ [9], Cu-As-Te [10] etc. A very high conductivity of the chalcogenide glasses, analogous to that in fast ion-conducting oxide glasses, exists in some Li-containing chalcogenide systems[11-12]. These glasses are well known for producing switching and memory devices.

Halide Glasses :

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)[13], AgX (X=Cl, Br, I)[14], alkali-fluoride-beryllium, Li-F glasses, iodine glasses etc.. Out of which iodine glasses have good far IR transmission and moisture resistance properties[15]

Spin Glasses :

Spin 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 generally referred to as the freezing temperature T_f. These materials are known as spin glasses. At temperature below T_g, the spins have no long-range magnetic order, but instead are found to have static or quasistatic orientation which vary randomly over macroscopic distances. The latter state is referred to as spin glass magnetic ordering. Spin glass ordering is usually detected by means of magnetic susceptibility measurements. Large number of spin glasses have been studied, such as cobalt and manganese-alumino-silicate, $Eu_xSr_{1-x}S$, $Au_{1-x}Fe_x$, Fe_xCr_{1-x}, $(Fe_{1-x}\text{-}Mn)_{0.75}$ $(P_{16}B_6Al_3)_{0.25}$, spin glasses, Cu-Ga_x-Al_x-$Fe_{2-2x}O_4$ [16], $KCo[Fe(CN)_6]$ [17], Tb_2TiO_7[18] etc.

Metallic Glasses :

Some of the metal alloys which can be produced in amorphous form by very rapid cooling (splat quenching technique) known as metallic glasses. They tend to 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. In 1960 the first true metallic glass, $Au_{80}Si_{20}$, an alloy containing 80 at. % Au and 20 at. % Si was obtained. Then after a number of metallic glasses were invented. Many workers studied the metallic glasses such as $Al_{90}Ni_6Nd_4$[19], Co-Nb-B-Cu[20], Al-Fe-Nb[21], Fe-P[22], Fe-Ni[23] etc. and studied their various properties like electrical conductivity, thermal properties, magnetic properties etc.

1.12 INORGANIC GLASSES:

Inorganic oxide glasses are the oldest and well known non-crystalline materials. These glasses have a great technical importance due to their versatile structure. There are number of inorganic glasses such as soda-lime silica, boro-siliate glasses. Alumino silicate, light barium crown, softsolder glasses, boro-vanadate glasses, photosensitive, photochromative glasses etc. Depending upon the use various types of glasses are available in present days.

In principle any substance, if cooled from the liquid state fast enough to prevent crystallization, can be made into a glass. However, only a limited member of oxides such as P_2O_5, B_2O_3, SiO_2, etc. have been made into glassy state at normal cooling rates, such as obtained by allowing the liquid to cool of its own from melting temperature to room temperature. In fact, to make them in crystalline state is a difficult task, these substance are known as *"glass formers"*. This is because of their high viscosity at the melting point.

The interatomic forces in glass 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 atom in glasses must form an extended three-dimensional network. However, the diffuseness of x-ray diffraction patterns of glasses shows that this network is not a periodic one i.e., glasses exhibit complete absence of long range order but possesses only the short range order. This order extends upto 10 to 20 Å.

According to the Zachriasen-Warren network theory[24-25], the following rules are valid for the formation of low order 3-dimensional networks; i.e., the glass formation of simple compounds such as SiO_2, B_2O_3, P_2O_5, As_2O_3 GeO_2, etc.

(i) An oxides or compound tends to form a glass if it easily forms polyhedral groups as smallest building units.

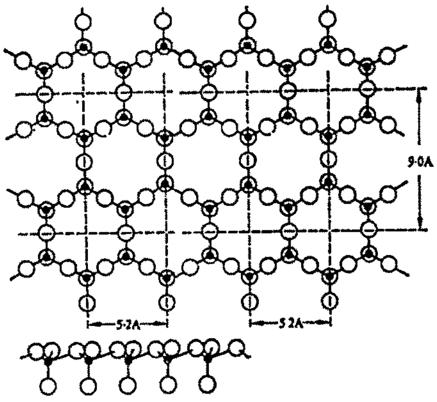
(ii) Polyhedra should not share more than one corner.

(iii) Anion (e.g. O^{-2}, S^{-2}, F^-) should not bind more than two central atoms of a polyhedron. Thus, in simple glasses anions form bridges between two polyhedra.

(iv) The number of corners of polyhedra must <6.

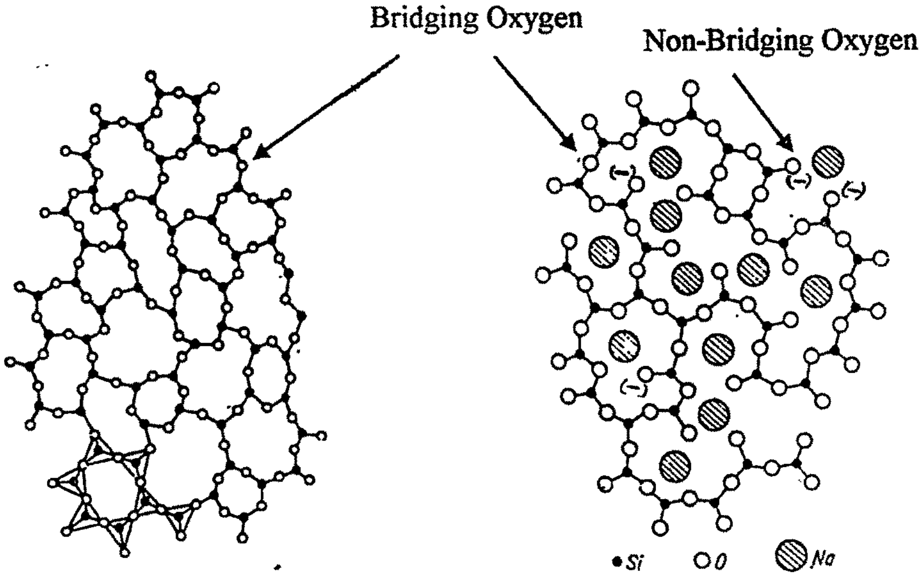
(v) At least three corners of a polyhedron must connect with neighbour polyhedra.

The oxides such as B_2O_3, SiO_2 etc. which form glasses satisfying the above rules (Figure 1.12 (a) and (b). These oxides are therefore, called *"glass formers" or "network formers"*. If a large cations such as K, Na, Ca, Ba are introduced into such simple glasses i.e., by melting SiO_2 and Na_2O or CaO- bridges are broken [Figure 1.12 (c) and (d)]. The oxygen (or other anion like S^{-2}, F^-) coming along with the large cation will assume the site at the free end of the separate tetrahedron, while the large cavity originating on the severance of the network at the sites. Thus, addition of alkali or alkaline earth oxides modifies the glass structure by making it more open. These oxides are therefore known as *"glass modifier"* or *"network modifier"*. Because of its large ionic radii, it ruptures the glass forming structure/polyhedras and restricts the mobility of the elements which constitute the arrangement during the time of cooling. It also produces the non-bridging oxygens (NBO) shown in Figure 1.12 (c). These oxygens atoms are connected with chains from one side and other bond remains free having more negative charge on it, whereas bridging oxygen is connected with the anions in the chains from two sides, and makes



(a)

Figure 1.12: (a) Regular periodic arrangement of atoms (or ions) in silicate (SiO_2).



(b) (c)

Figure 1.12: **(b)** Disordered netting of SiO_4 building blocks in SiO_2 glass (Quartz glass).
(c) Arrangement of atoms (or ions) in a sodium silicate glass. When Na_2O is incorporated, the large sodium ions rupture the oxygen bridges and open (modify) the structures.

bridge. The material when cooled quickly enough to suppress nucleation and growth of crystal gives to formation of a glassy state and has an x-ray short range order.

1.13. BORATE STRUCTURE AND BORON ANOMALY:

The structure of B_2O_3 glass as shown by early x-ray studies consists of BO_3 triangular units with boron at the center and three oxygens at the corners of an equilateral triangle. These BO_3 units are connected randomly with one another in such a way that each oxygen is connected (bridged) between two borons and oxygens are thus called "bridging oxygen" [26-27].[Figure 1.13(a)]. Krogh-Moe[28] deduced from nuclear magnetic resonance, infrared and Raman spectra and other physical properties that these BO_3 triangles form the 'boroxol' group. This group is six numbered planar ring containing alternatively boron and oxygen atoms. Within these rings, the B-O-B angle is 120° while between the rings is 130°, with a random orientation of the linked rings about this bond in the glass-network. The work of x-ray fluorescence excitation by Warren and Mozzi [26] was in agreement with the model of linked rings, although, a better agreement was possible by assuming that a small part of BO_3 groups was linked randomly to the boroxol groups and was not in rings.

Addition of network modifiers changes the structure of the glass. Such glasses are represented by formula $xMeO: (1-x)B_2O_3$, where x is the mole fraction of network modifying metal oxide MeO such as K_2O, Na_2O, BaO etc. Various x-ray, infrared, nuclear magnetic resonance studies have shown the following structural features with increase in x.

(i) For $x=0$, only BO_3 units are present, i.e., boron is found in 3-fold coordination with oxygens; all oxygens being *'bridging'* ones.

(ii) With increase of x for $x>0$, a number of BO_4 units are invariably

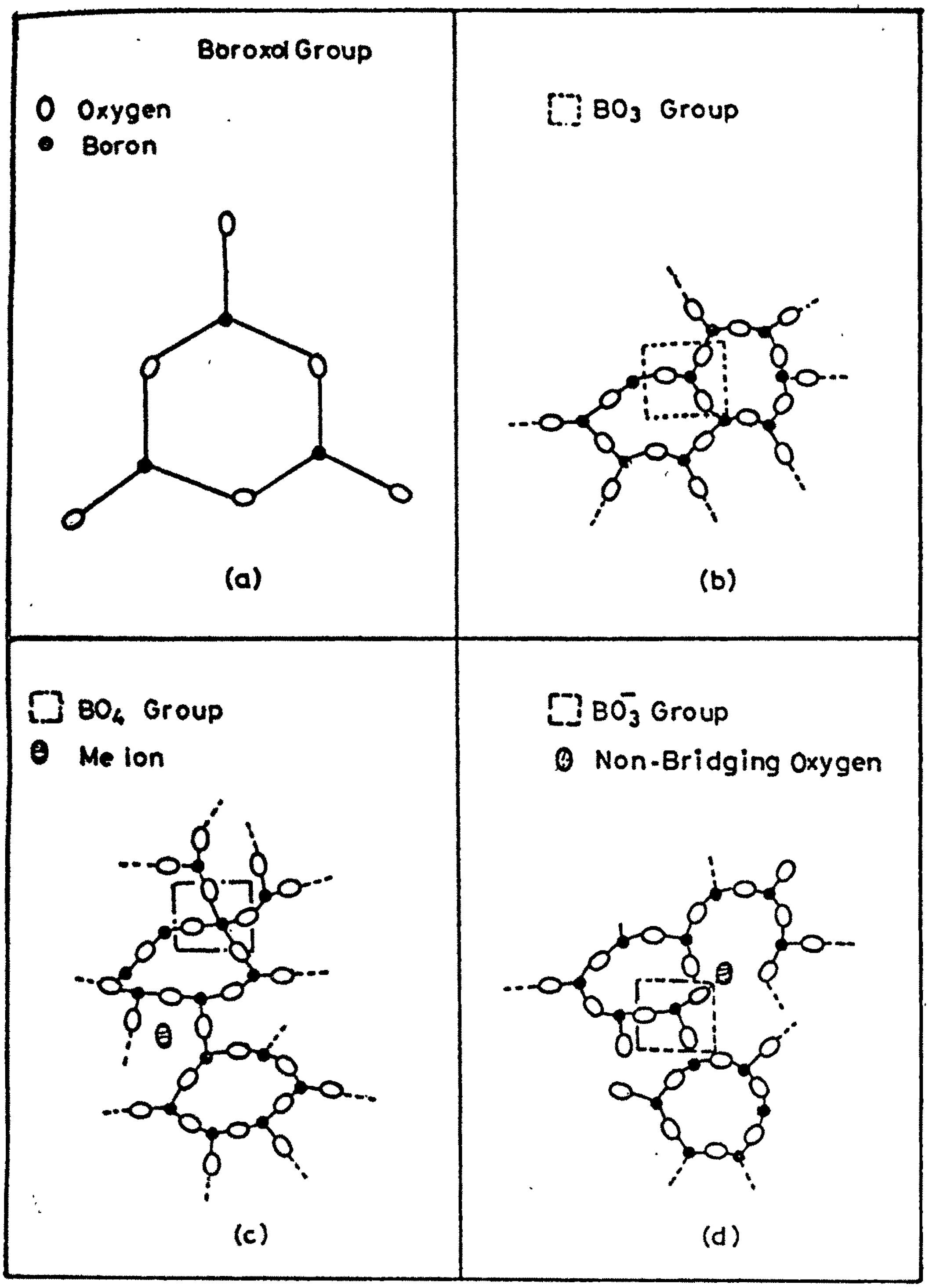


Figure 1.13: Schematic diagram of various structural units.

formed. BO_4 units consist of tetrahedron of oxygens with boron at its center, i.e., boron is four-fold coordinated with oxygens.

(iii) Fraction of four-fold coordinated borons, N_4, first increases, reaches a maximum and thereafter decreases with increase in x (Figure 1.14).

(iv) For further increase of metal oxide, a number of BO_3^- units start appearing. BO_3^- is the triangular unit with one of the oxygens being *'non-bridging'*. The non-bridging oxygen means the one at the corner of a BO_3 unit which is neither connected to another BO_3 unit nor to BO_4 unit, but connected to the metal ion.

(iv) The number of BO_3^- units is zero for $x<x_o$ and increases continuously with x for $x>x_o$; where $x_o\sim 0.17$ for monovalent network modifiers.

The various structural units; BO_3, BO_4 and BO_3^- are shown in Figure 1.13.

Boron Anomaly:

Addition of network-modifier in borate glasses brings out structural changes which are responsible for its unique physical properties. Some physical properties exhibit maximum while others show a minimum or a marked change at $x\sim x_o$ (Figure 1.14). These abnormal properties exhibited by borate glasses are not shown by other oxide glasses such as phosphate, vanadate and silicate. This deviation from normal behaviour at a certain composition is known as boron anomaly. The word 'anomaly' is used because some properties exhibit maximum while others minimum and others show a marked change near some particular composition. The marked change is observed in the position of the ultraviolet absorption edge as a function of x at $x\sim x_o$. The coefficient of thermal expansion exhibit minimum. The example of

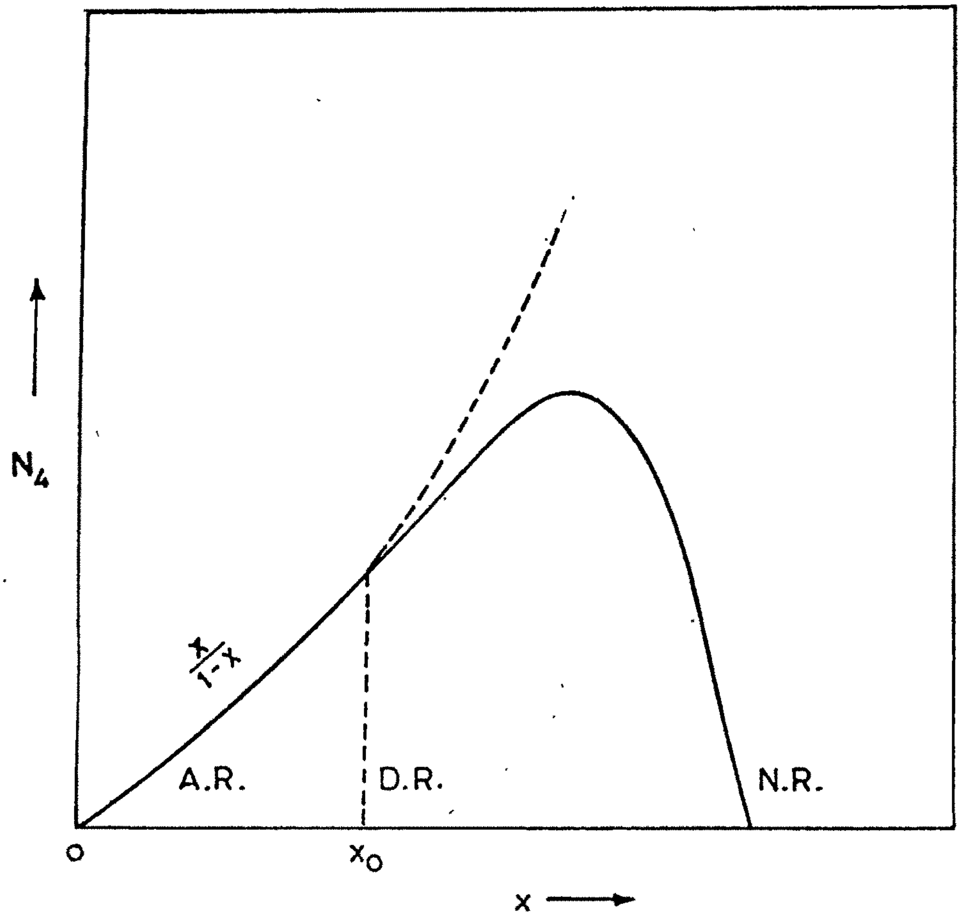


Figure 1.14: Variation of N_4 with x in xMeO: $(1-x)B_2O_3$ glass.

a property which shows a maximum at a certain composition is the number of BO_4 units present in the borate glasses doped with some modifying oxide.

Because of the above mentioned interesting properties and the fact that B_2O_3 is important ingredient in a large number of commercial glasses, the study of borate glasses continues to be special scientific and technological interest.

1.14. Vanadium Structure:

Transition metal oxides (TMO) have a number of particular properties and have been studied extensively. The vanadium oxides are important in many respects, because they exhibit useful metal-insulator or semiconductor-metal transition as a function of temperature and pressure.

The V_2O_5 structure has been determined by Bachmann, Ahmed and Barnes [29]. 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 (Figure 1.15), wherein the shortest distance corresponds to a double vanadyl-bond (VO_1=1.585 Å). The longest V-O distance ($V\text{-}O_1{}'$= 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.[Figure 1.15(b) and 1.16 (a) and (b)] The other V-O distances are shown on Figure 1.15.

The greatest promise for utilization lies in the electrical properties of vanadate glasses. They have recognized as electronic semiconductors [30-32]. Semiconductivity is attributed due to the electron transition between different states of valency, such as $V^{+4}\rightarrow V^{+5}$ transitions.

Because of the above-mentioned interesting properties and the fact that B_2O_3 and V_2O_5 are important ingredients in a large number of commercial glasses, the study of borate glasses continues to be of special scientific and technological interest. The borate glasses have been systematically studied

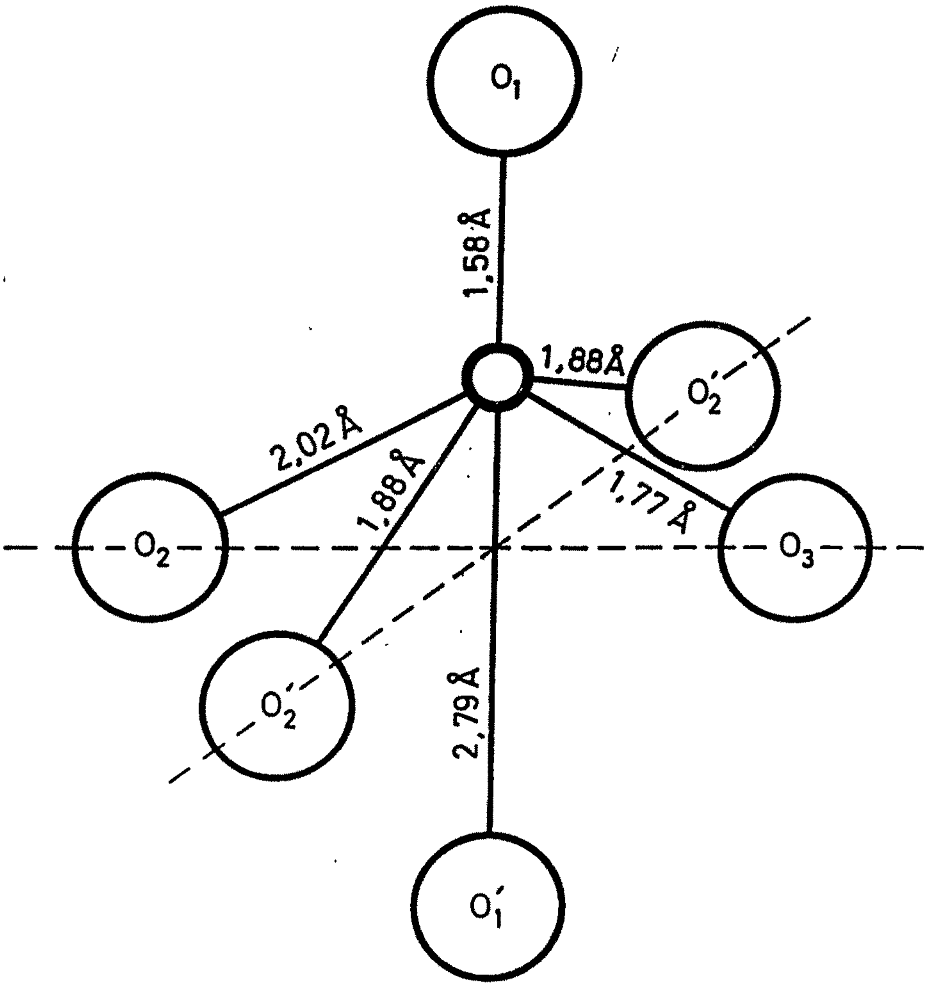


Figure 1.15: (a) Building block of the V_2O_5 structure showing the different V-O distances in the deformed octahedron.

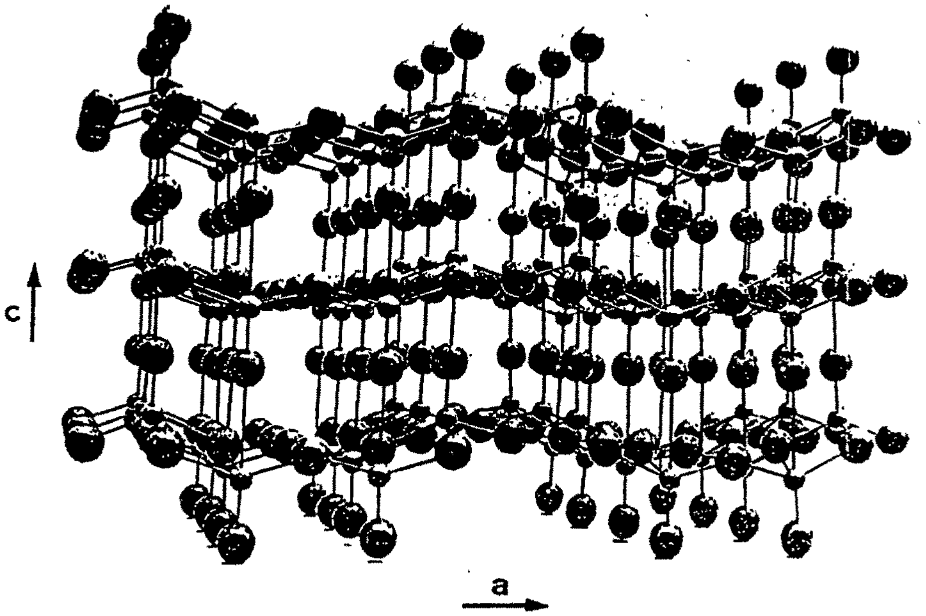


Figure 1.15: **(b)** Model of the V_2O_5 structure, the a-direction being in the plane of the figure. The large spheres represent oxygen ions, the smaller ones vanadium ions.

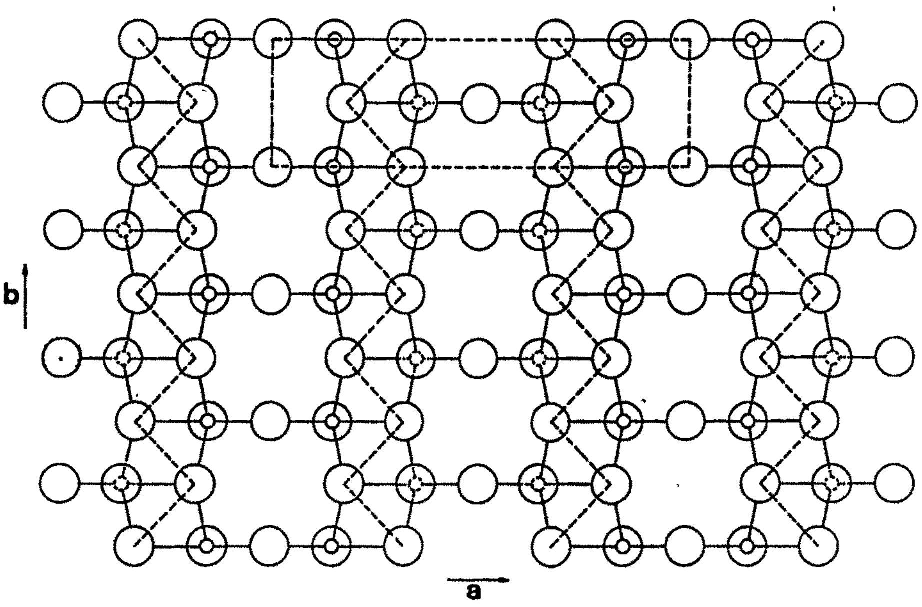


Figure 1.16: (a) Projection of the V_2O_5 structure on the c-plane. The rectangular unit mesh in this plane is also indicated.

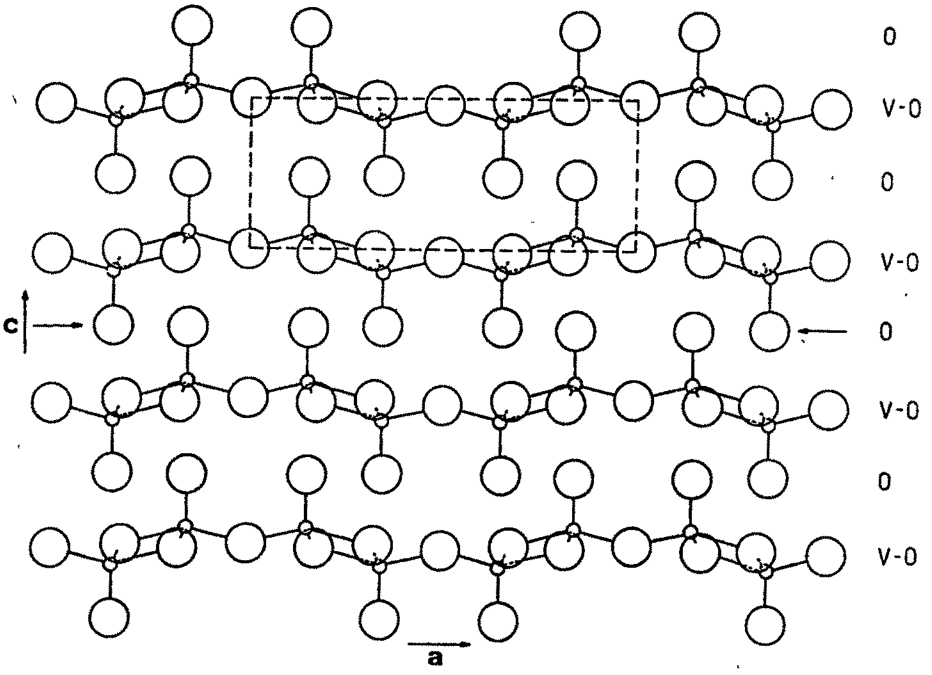


Figure 1.16: (b) Projection of the V_2O_5 structure on the b-plane.

using various techniques such as Mössbauer , infrared, dc conductivity and differential thermal analysis in the present work.

Most of the borate glasses are insulating in nature. The addition of transition metal oxides (TMO) such as V_2O_5, Fe_2O_3, CuO etc. makes these glasses semiconducting in nature. The semiconducting glasses have attracted scientific interest and technical applications.

Therefore, Potassium Boro-Vanadate-Iron glass system has been chosen for the present study. Iron oxide has been added as a Mössbauer probe. An attempt has been made to understand the effect of glass modifier K_2O and glass former V_2O_5 and Mössbauer probe Fe_2O_3 by using various techniques like Mössbauer Spectroscopy, IR-spectroscopy, DC conductivity, Thermal & electrical switching properties thermoelectric power and characterization of glasses using X-ray, DSC, density measurements and chemical analysis. The following three series of glass systems have been prepared and discussed in the present thesis.

(i) $xK_2O:(95-x)(2V_2O_5 : B_2O_3) : 5\ Fe_2O_3$, where x= 0,5, . . . 30 in step of 5.
(ii) $20K_2O : yV_2O_5 :(75-y)B_2O_3 : 5\ Fe_2O_3$, where y= 40 to 75 in step of 5.
(iii) $xK_2O:(100-x-y)[(1+n)V_2O_5 :B_2O_3]:y\ Fe_2O_3$, where x= 0 to 20 in step of 5. y= 5 to 15 in step of 2.5. and n = 0.2 to 1 in step of 0.2.

REFERENCES:

1. Materials Advisory Board, Nat. Acad. Sci. Res. Council MAB-243(1968)
2. G.W. Morey, Properties of glass, Reinhold publishing Corp., New York (1954)
3. G.O.Jones, 'Glass', Nethuen, London, 1956, p. 1.
4. Flaschen S. S., A. D. Pearson, W. R. Northover, J. Amm.Cerm. Soc. **42**(1959)450.
5. Borisova Z. U., V. R. Panus, A. A. Obrazotsov, Vestnik Liningr Univ. Ser Fiz. I. Khim H. **22**(1970)121.
6. Linke D., G. Eberhardt, Q. Dietz, Proceeding 6th International Konfer amorph. Halbl. Leningrad 1975, 251-255.
7. Feltz A. L., Senf. Z. Chem **15**(1975)119.
8. T. Wagner, So. Kasap, J. of Non-Cryst. Solids Vol **227-230** (1998)752.
9. S. Murugavel, S. A. Sokan, Phy. Rev. B. Cond. Matter, Vol. **58**, No.6(1998)3022.
10. M. Ohoto, K. Tanaka, J. of Non-Cryst. Solids Vol **227-230**, (1998)784.
11. Malugani J. P., & G. Robert Solid State Ionics **1**(1980)p. 519.
12. Mercier R., J. P. Malugani, B. Fahys & G. Robert, Solid State Ionics **5**(1981)663.
13. A. Kriltz, M. Muller, Mol. Cryst. Liq. Cryst. Vol.**297-298**(1997)23.
14. K. Kadono, M. Shojiya, H. Kageyama, N. Kamijo, Y. Kawamoto, H. Tanaka, J. Phy. Cond. Matter (UK) Vol. **10**, No. 23 (1998) 5007.
15. Cooper E. & C. Angell, J. Non-Cryst. Solids **56**(1983)75.
16. L. G. Antoshina, A. N. Goryaga, J. of Magn Magn. Mater, Vol. **188**, No. 1-2 (1998)p.228.
17. T. Wasiutynski, Z. Szeglowski, A. W. Pacyona, Physics B. Vol. 253, No. 3-4(1998)305.

18. B. D. Gaulin, J. S. Gardner, Physics B. Vol. **241-243** (1997)p. 511-516.
19. M. Calin, U. Koester, Mater. Sci. Forum (switz) Vol. **269-272**(1998)749.
20. A. Slawska-Waniewska, L. Malkinski, A. Wisniewski, H. K. Lachowicz, Mater. Sci. Forum (switz) Vol. **269-272**(1998)871.
21. F. Audobert, S. Vazquez, Mater. Sci. Forum (switz) Vol. **269-272**(1998)837.
22. M. Takashi, M. Koshimura, J. Appl. Phys(Jpn) Vol. **18**, No.3 (1979)685.
23. M. Stubicar, J. Mater Sci. Vol. **14**, No. 5 (1979)1245.
24. Zachariasen W. J., J. of Amm. Cerm. Soc. **54**(1932)3841.
25. Warren B. E., W. L. Bragg, Z. Krist, **69**(1928)168.
26. B. L. Mozzi and B. E. Warren, J. Appl. Cryst. 3(1970)251.
27. P. H. Bray, J. of Chem. Phys. **29**(1984)1958.
28. J. Krogh-Moe, J. of Non-Cryst. Solids **1**(1969)269.
29. H. G. Bachmann, F. R. Ahmed & W. H. Barnes, Z. Krist. **115**(1961)110.
30. Denton E. P., H. Rawson, Nature **173**(1954)1030.
31. Baynton P.L., H. Rawson, J. E. Stanwerth, J. of Electrochem.Soc. **104**(1957)237.
32. Mackenzie J. D., Modern Aspects of the Vitreous state, Butterworths, London, 1960.