CHAPTER-2
PREPARATION AND CHARACTERIZATION

2.1 INTRODUCTION

The preparation and characterization of glasses are important steps in understanding the structure and properties. There are a number of techniques [1] which are used for the synthesis of glasses. The commonly used methods to produce the non-crystalline material for commercial as well as academic interest are (i) melt quenching, (ii) thermal evaporation (iii) sputtering (iv) glow discharge and (v) chemical deposition. Among these the oldest ever method is the melt quenching method, which requires rapid cooling of melt called quenching. The property of glass prepared by melt quenching depends on a number of variables namely composition, melt volume, type of quenching, quenching temperature and melt history [2]. These variables combine to yield a quenching rate, which may or may not be sufficient for a given melt to suppress crystallization when cooled and thus transform to a vitreous state through a reversible increase of viscosity. It is well known that the various properties of the material for example electrical, dielectric, magnetic, mechanical etc. are quite sensitive to the mode of material preparation.

Phosphate glasses find variety of applications. P₂O₅ is one of the classic glass forming oxide. Glasses can be formed over a large composition range when added with alkali and alkaline earth oxides [3]. Large areas of glass forming region exists in polynary combinations containing P₂O₅, V₂O₅, B₂O₃ and TeO₂ etc.

In glasses containing two glass formers such as P₂O₅ and V₂O₅, the coordination numbers and connectivities (number of bridging oxygen atoms in coordination) of both
phosphate and vanadate species can vary in a complex manner as a consequence of modification when a modifier oxide is added to the glass. Modification is generally understood to be the reaction of $O^{2-}$ ions, which results in structural changes including creation of non-bridging oxygens being the first step. The complex structural changes are critically determined by chemical factors such as hierarchy of bond energies, reaction properties of structural units towards $O^{2-}$ ions and chemical stabilities of the resulting structural entities. It is therefore important to examine the consequence of $O^{2-}$ ion (modification) to the phospho-vanadate network.

The following sections we describe the preparation and characterization of various glass systems used for further investigations. These glass systems are synthesized by melt quenching technique and are characterized by X-ray diffraction, glass transition temperature, density and molar volume.

I  ZINC- VANADO-PHOSPHATE GLASSES

1) $x$ ZnO-(80-x) V$_2$O$_5$-20P$_2$O$_5$ [LP], (LP= Low Phosphate glass)
2) $x$ ZnO-(60-x) V$_2$O$_5$-40P$_2$O$_5$ [HP], (HP= High Phosphate glass)

(where $x = 10, 20, 30, 40$ and $50$ in mol%)

II  SILVER- PHOSPHO-VANADATE GLASSES

1) $x$ Ag$_2$O- (50-x) P$_2$O$_5$-50V$_2$O$_5$

(where $x = 5, 10, 15, 20, 30$ and $40$ mol%).

2.2 SAMPLE PREPARATION

Samples were synthesized using analytical grade ammonium dihydrogen orthophosphate (NH$_4$H$_2$PO$_4$), vanadium pentoxide (V$_2$O$_5$), zinc oxide (ZnO), and silver oxide (Ag$_2$O) as starting materials. The components were weighed in appropriate
amounts, mixed and ground. The mixtures were then melted in a porcelain crucible placed in a muffle furnace. Initially the mixture was kept in furnace at 400\(^\circ\)C to remove NH\(_4\) and water vapour, then the furnace temperature was set to 800-1000\(^\circ\)C depending upon the composition. The melts were kept in the furnace for about 30 minutes for homogenization and then quickly pressed between polished brass blocks. The resulting glass samples were of various sizes and about 1-2 mm in thickness. The glass samples were annealed below the glass transition temperature for about an hour and then cooled to room temperature. Some of the samples were hygroscopic, and hence all the samples were preserved in a desiccator.

2.2.1 X-ray diffraction studies

The X-ray diffraction pattern of the material gives the identification of the constituent phases present in the material. It gives the information about the state of combination of chemical elements presents in the mixture and also about the formation of compound if any, as a result of the individual constituents.

All the samples were studied by X-ray diffraction using a X-ray diffractometer (model Rigaku DMAX-1C) employing Cr-K\(\alpha\) radiation. Some of the typical diffractograms of the compositions are shown in figures (2.1a to 2.1b). From the figure, it was found that the samples did not show sharp peaks, indicating that they are amorphous in nature.

2.2.2 Glass transition temperature

Glass transition temperatures, \(T_g\) of the glasses were measured using Perkin-Elmer DSC-2 differential scanning calorimeter. The glass samples were prepared for DSC by cutting the glass into small pieces of disks. By heating the glass samples at the
Fig. 2.1 Typical X-ray diffractograms
rate of 20°/min, the DSC results were obtained. Care was taken to reduce the thermal drift by pre-warming the instrument in the temperature range of interest. Glass pieces weighing 40 to 50 mg were hermetically sealed in aluminium pans and were annealed near the glass transition temperature (which was identified from an initial scanning) for 30 minutes and cooled to 100 K below \( T_g \) at the rate of 20 K/min. \( T_g \) was determined at the intersection of extrapolated linear portions around the glass transition region. The glass compositions and \( T_g \) values are shown in tables 2.1 to 2.3.

2.2.3 Density and molar volume

The densities of glasses free from any air bubbles were measured by the method of Archimedes using benzene as an immersion liquid (density = 0.879 g/m\(^3\)) at room temperature. The density values are accurate to ± 0.005 g/m\(^3\). The molar volume was calculated by using the relation \( V_m = \frac{M}{\rho} \) where \( M \) is the molecular weight of the glass composition and \( \rho \) is the density of the glass.

2.3 RESULTS AND DISCUSSION

2.3.1 Glass transition temperature of ZnO-V\(_2\)O\(_5\)-P\(_2\)O\(_5\) glasses

The typical thermograms for few selected compositions are shown in figure 2.2. Figure 2.3 shows the variation of \( T_g \) versus ZnO concentration (solid lines are guide to eye). As can be seen from the figure 2.3 that both LP and HP glasses, the \( T_g \) increases with increase of ZnO concentration. Secondly, the \( T_g \) of HP glasses are higher than those of LP glasses. Normally, one would expect the \( T_g \) of host glasses to decrease with increase of modifier oxide due to network degradation. However, in Zinc-Vanado-Phosphate glasses, the \( T_g \) increases with modifier oxide (ZnO). This behaviour can be
Fig. 2.2 Typical thermograms (DSC)
Figure 2.3 Variation of $T_g$ versus mol\% ZnO for both LP and HP glasses
explained qualitatively by taking into consideration of the role of \( \text{Zn}^{2+} \) in cross-links of different phosphate chains. \( T_g \) of phosphate glasses not only depend upon degradation of P-O-P linkage due to addition of ZnO, but also depend upon the nature and type of the cation present. According to Hudgens and Martin [4] the \( T_g \) would increases with increase of modifier if the modifier ion occupies the cross-link position in phosphate chains. In \( x\text{Li}_2\text{O}-(1-x) \text{P}_2\text{O}_5 \) glasses they have observed that for \( \text{Li}_2\text{O} \) concentration \( \cdot 33 \) mol\%. \( T_g \) progressively increases with increase of \( \text{Li}_2\text{O} \). The increase in \( T_g \) even though the fraction of non-bridging oxygens is increasing is explained in terms of an increasing entanglement of long chain of \( \text{PO}_2 \) groups. They have further shown that \( T_g \) not only depend upon chain entanglement but also depend upon the nature and type of cation. For example, if an alkali ion is replaced by a divalent alkaline earth ion of same radius but double the charge, then the cation can cross-link between the two phosphate chains and hence the \( T_g \) will increase substantially. Figure 2.4 shows the proposed model (Hudgens and Martin [4]) of cross-linking effects of (\( \text{Li}^+ \), \( \text{Mg}^{2+} \), \( \text{Al}^{3+} \)) and possible \( \text{Zn}^{2+} \) positions are also shown.

2.3.2 Density and molar volumes of the \( \text{ZnO- \text{P}_2\text{O}_5 - \text{V}_2\text{O}_5} \) glasses

Table 2.1 and 2.2 shows the composition, density and molar volume of the \( \text{ZnO-P}_2\text{O}_5-\text{V}_2\text{O}_5 \) glasses. Figures 2.5a and 2.5b shows the variation of density versus \( \text{ZnO} \) mol\% for LP and HP glasses respectively and figures 2.5c and 2.5d represents the molar volume versus mol\% of \( \text{ZnO} \) for LP and HP glasses respectively.

The density of LP and HP glasses were found to lie in the range of 3.11 to 3.62 gm/cm\(^3\) and 2.96 to 3.56 gm/cm\(^3\) respectively. As can be seen from the figure 2.5a that in LP glasses initially the density increases slowly (upto 30 mol\% of \( \text{ZnO} \)) and more
Fig. 2.4 Cross linking effects of \( \text{Li}^+, \text{Mg}^{2+}, \text{Al}^{3+} \) and \( \text{Zn}^{2+} \)
rapidly with further increase of ZnO mol\% . In case of HP glasses (see figure 2b) the
density increases monotonically up to 30 mol\% of ZnO and further increase of ZnO does
not affect the densities much.

**Table 2.1 xZnO-(80-x)V_2O_5-20P_2O_5 glasses**

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<th>SL No</th>
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<th>V_2O_5 mol%</th>
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**Table 2.2 xZnO-(60-x)V_2O_5-40P_2O_5 glasses**

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Figure 2.5a Variation of Density versus ZnO mol\% in LP Glasses
Figure 2.5b Variation of Density versus ZnO mol% of HP Glasses.
The variation of molar volumes in LP and HP glasses are shown in figures 2.5c and 2.5d. The values of the molar volumes were found to lie in the range of 30 to 55 cm$^3$. As can be seen from the figures 2.5c and 2.5d, the molar volumes decrease monotonically with increase in mol% of ZnO. This is to be expected since the total number of oxygen atoms in the molar composition of the glasses decrease when V$_2$O$_5$ is substituted by ZnO.

It is instructive to see if the molar volume of these glasses can be compared with the random close packed (RCP) volume of the oxide ions present (oxide ion radius 1.36Å$^0$). Zn$^{2+}$, P$^{5+}$ and V$^{5+}$ ions may be considered as simply embedded in the voids of the RCP assembly of O$^{2-}$ ions. Since RCP results in the formation of tetrahedral voids almost exclusively and the radius of the embedded ion can be at the most 0.3Å$^0$ (0.22x1.36Å$^0$). Therefore it can accommodate the P$^{5+}$ and V$^{5+}$ ions (radius 0.35Å$^0$ and 0.59Å$^0$ respectively) because of the fluffiness of O$^{2-}$ ions. However, Zn$^{2+}$ ion (radius 0.74 Å$^0$) can be expected to expand the random close packed assembly of oxide ions. The four surrounding ions can be assumed to move outwards isotropically. To a first approximation, this expansion due to the insertion of one mole of Zn$^{2+}$ ions can be treated as a corrective volume of

$$(4\pi/3)[(\sqrt{3}a/2 + (0.74-0.3))^{1/3} - (\sqrt{3}a/2)^{1/3}] \times 10^{-24}(4.6N/4) \times 13.678 \text{ cc}$$

where $\sqrt{2}a$ is the inter oxygen ion distance and N is the Avogadro number. The last factor of (4.6N/4) is introduced because not all oxygen cages are independent. Therefore the increase in volume “per oxygen” will be

$$(4\pi/3)[(\sqrt{3}a/2 + (0.74-0.3))^{1/3} - (\sqrt{3}a/2)^{1/3}] \times 10^{-24}/4 \text{ cc}$$

and for the 4.6N oxygens, it is multiplied by 4.6N. Thus the RCP volume of the ZnO glasses (with packing fraction 0.63) should be
Figure 2 5c Variation of Molar Volume versus ZnO mol% in LP Glasses
Figure 2.5d Variation of Molar Volume versus ZnO mol% in HP Glasses
4.6 (4π/3)N (1.36)^3 \times 10^{-24} \times 0.63 + 13.6781 = 60.00 \text{ cc}

This is slightly higher than the observed molar volume of 52.53 cc (10ZnO-20P_2O_5-70V_2O_5).

Therefore molar volume suggest that the long chains intervene so as to give rise to fairly close positioning of the oxide ions, although the large sizes of Zn^{2+} ions (larger than the voids), P-O-P angles (which ranges between 120 and 180 degree) [6] and O'-O' Coulombic repulsions prevent the dense as the (imaginary) RCP structure of only O^{2-} ions (30.22 cc).

2.3.3 Glass transition temperature of Ag_2O-P_2O_5-V_2O_5 glasses

Figure 2.6 shows the variation of glass transition temperature versus mol\% of Ag_2O of silver-vanado-phosphate glasses. As can be seen from the figure 2.6 the T_g decrease with increase in mol\% of Ag_2O. The behaviour of T_g as a function of Ag_2O can be understood as a result of structural changes occurring in phosphate groups. The addition of Ag_2O results in the formation of non-bridging oxygens and progressive degradation of ultraphosphate [POO_3/2]^0 to metaphosphate [POO_2/3O]^1, pyrophosphate [POO_1/2O_2]^2 and orthophosphate [POO_1]^3 groups. The results obtained are consistent with the behaviour of T_g in other phosphate glasses [5].

2.3.4 Density and molar volumes of the Ag_2O-P_2O_5-V_2O_5 glasses

Table 2.3 shows the values of density and molar volume of Ag_2O-P_2O_5-V_2O_5 glasses. The densities of these glasses were found to lie in the range of 3.02 g/cm\(^3\) to 5.04 g/cm\(^3\). Figure 2.7 shows the variation density versus Ag_2O concentration. As can be seen from the figure 2.7, the density increases slowly upto 20 mol\% Ag_2O and with further increase of Ag_2O, the density increases significantly.
Figure 2.6 Variation of $T_g$ versus mol% of Ag$_2$O in Ag$_2$O-P$_2$O$_5$-V$_2$O$_5$ Glasses
Figure 2.7 Variation of Density versus mol\% of Ag$_2$O in Ag$_2$O-P$_2$O$_5$-V$_2$O$_5$ Glasses
Figure 2.8 Variation of Molar Volume versus mol% of Ag$_2$O in Ag$_2$O-P$_2$O$_5$-V$_2$O$_5$ Glasses
Table 2.3 xAg<sub>2</sub>O-(50-x)P<sub>2</sub>O<sub>5</sub>-50V<sub>2</sub>O<sub>5</sub> glasses

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The calculated molar volume is in the range of 38.52 cm<sup>3</sup> to 55 cm<sup>3</sup> and was found to decreases monotonically with increase in concentration of modifier oxide (Ag<sub>2</sub>O mol%) as shown in figure 2.8. The molar volumes of silver based glasses were quite high compared to the calculated RCP volume (see table 2.3). This indicates that Ag-based glasses are some what more ordered in their structure. This is what one would expect if cluster-tissue texture were assumed to be present in such glasses with the structures of clusters being dominated by crystalline order [7].

CONCLUSIONS

ZnO-V<sub>2</sub>O<sub>5</sub>-P<sub>2</sub>O<sub>5</sub> and Ag<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub>-P<sub>2</sub>O<sub>5</sub> glasses have been synthesized by melt quenching techniques and were characterized by X-ray diffraction and by the measurement of glass transition temperature. In ZnO-V<sub>2</sub>O<sub>5</sub>-P<sub>2</sub>O<sub>5</sub> glasses I<sub>g</sub> increases gradually with increase of ZnO. This variation is explained on the basis of position of
Zn$^{+}$ cross-linking the phosphate chains. The $T_g$ in Ag$_2$O-V$_2$O$_5$-P$_2$O$_5$ glasses decreases with increase of Ag$_2$O concentration as expected. Densities and molar volumes also change systematically in both the glass systems.
REFERENCES


