CHAPTER-3

Part-B Present Study

DC ELECTRONIC CONDUCTIVITY, IR, EPR AND MAS-NMR
STUDIES OF ZINC-VANADO-PHOSPHATE GLASSES.

3.1B INTRODUCTION

Phosphate glasses are of technological interest due to their superior physical properties such as high thermal expansion coefficients, low melting temperature and low softening temperature [51-56]. Unfortunately, such low melting point glasses usually exhibit less durability than equivalent silicate glasses and in general, the hygroscopic nature of such glasses prevents them from replacing more conventional glasses in most practical applications [57-60]. Therefore, here we have used the conditional glass former V$_2$O$_5$ to prevent the hygroscopic nature of the glass and secondly, to understand the structural role of ZnO in vanado-phosphate glasses since such oxides known to occupy both in network modifying and forming positions in the glass network. For example, the structural role of PbO in phosphate glass structure is complex and it is observed that with increasing the content of PbO, it may act as a glass former [61,62] and glass modifier [63,64]. In some cases ZnO also seem to exhibit dual nature [65,66]. To understand the relationship between properties and structure of these glasses, we have used the different techniques such as dc conductivity, IR, EPR, and MAS-NMR in the present study.
3.2B EXPERIMENTAL PROCEDURE

The following two series of glasses were synthesised.

i) $x\text{ZnO-}(80-x)\text{V}_2\text{O}_5\text{-}20\text{P}_2\text{O}_5$ \[LP\] and

ii) $x\text{ZnO-}(60-x)\text{V}_2\text{O}_5\text{-}40\text{P}_2\text{O}_5$ \[HP\]

where $x = 10, 20, 30, 40, \text{ and } 50$ in mol\% (in LP series glasses with 15 mol\% and 25 mol\% were also studied). Samples were prepared using melt quenching method. Details of preparation and characterisation have been already described in Chapter 2. 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. For electrical measurements suitable samples with dimension $10\times10\times2$ mm$^3$ were selected. A sample holder used for the dc electrical measurements is shown in figure 3.1. The resistance of the sample was measured by applying a dc field of 1V and the current through the sample was measured using a digital electrometer (ECIL EA-5600). The temperature was measured by using a chromel-alumel thermocouple placed very close to the sample. The temperature dependence of conductivity of these systems was studied in the temperature range 360-520K. Measurements were made repeatedly and with changed polarity of the applied voltages, although there was no a priori reason to suspect effect of polarization. The reproducibility was well within the experimental errors.

3.3B CONDUCTIVITY

Figures 3.2 and 3.3 show the variation of log $\sigma$ versus $(1000/T)$ for LP and HP glasses respectively (solid line is only a guide to eye). As can be seen from the
Fig. 3.1 Schematic diagram of the sample holder used for conductivity measurements.
Figure 3.2 Variation of log (σ) versus 1000/T in LP Glasses
Figure 3.3 Variation of log ($\sigma$) versus 1000/T in HP Glasses
Figures log (σ) increases with increasing temperature. The values of log (σ) were found to be lie in the range of $10^{-5}$ to $10^{-9}$ ohm$^{-1}$cm$^{-1}$ typical of glasses containing vanadium [8]. The plots of glasses with 30 and 50 mol% ZnO are not shown in figure as the values log (σ) of 30, 40 and 50 mol% ZnO show large overlap. Measurements were also made on binary 50V$_2$O$_5$-50P$_2$O$_5$ glass to study the effect of ZnO in these glass systems. The values of log (σ) were found to be of the order of $10^{-3}$ to $10^{-6}$ ohm$^{-1}$ cm$^{-1}$; about two order magnitude higher than glasses containing ZnO.

In semiconducting V$_2$O$_5$ doped glasses, the conductivity has been known to increase with increase of vanadium concentration [68,72] and this is attributed to both decrease in the V-V distance and to the increase in redox ratio (V$^{4+}$/V$^{5+}$) [2,4]. In HP glasses also log (σ) versus V$_2$O$_5$ concentration exhibit similar variation. However, we may notice that in LP glasses the conductivity of the glass with 40 mol% V$_2$O$_5$ is higher than that with 60 mol% V$_2$O$_5$. Since the other oxide present in the glass is ZnO, it appears that at 20 mol% concentration ZnO may bring about some special structural features which affect the conductivities in the manner observed in figures 3.2 and 3.3. We therefore examine this aspect by considering the various structural groups, which are likely to form in these glasses.

In these glasses, V$_2$O$_5$ and P$_2$O$_5$ are known to be glass formers. However, ZnO can behave both as a network former and as a network modifier. We first consider the modifier role of ZnO. P$_2$O$_5$ and ZnO can be represented as

$$\text{P}_2\text{O}_5 \equiv 2[\text{POO}_{3/2}]^0$$

$$\text{ZnO} \rightarrow \text{Zn}^{2+} + \text{O}^{2-}$$
The modification of \( \text{P}_2\text{O}_5 \) can be written as

\[
2[\text{POO}_{3/2}]^0 + \text{O}^{2-} \rightarrow 2[\text{POO}_{2/2} \text{O}]^-
\]

\[
\text{P}_2\text{O}_5 + \text{O}^{2-} \rightarrow 2\text{PO}_3^-
\]

The modification of \( \text{V}_2\text{O}_5 \) can be represented similarly

\[
2[\text{VOO}_{3/2}]^0 + \text{O}^{2-} \rightarrow 2[\text{VOO}_{2/2} \text{O}]^-
\]

\[
\text{V}_2\text{O}_5 + \text{O}^{2-} \rightarrow 2\text{VO}_3^-
\]

where \( \text{V}_2\text{O}_5 \) is considered as \([\text{VOO}_{3/2}]^0 \) units analogous to \([\text{POO}_{3/2}]^0 \) units.

Since the glasses consists of continuous and connected network of \([\text{POO}_{3/2}]^0 \) and \([\text{VOO}_{3/2}]^0 \) units, we may represent the modification even more meaningfully as

\[
\frac{1}{2}(\text{P}_2\text{O}_5 \cdot \text{V}_2\text{O}_5) + \text{O}^{2-} \rightarrow \text{PO}_3^- + \text{VO}_3^-
\]

\[
[\text{POO}_{3/2} \cdot \text{VOO}_{3/2}]^0 + \text{O}^{2-} \rightarrow [\text{POO}_{2/2} \text{O}]^- + [\text{VOO}_{2/2} \text{O}]^-
\]

(3.4B)

(where a breaking up of a P-O-V link is implied in the reaction (3.4B)

Even more importantly for the problem of electronic conductivity, we consider the following reactions, which occur at the high temperatures of the glass forming melts before quenching.

\[
\text{O}^{2-} \rightarrow 1/2 \text{O}_2 + 2\text{e}^-
\]

(3.5B)

(This represents loss of oxygen step)

\[
2\text{e}^- + 2[\text{V}''\text{OO}_{3/2}]^0 \rightarrow 2[\text{V}''\text{OO}_{3/2}]^2^-
\]

(3.6B)

(This represents \( \text{V}'' \rightarrow \text{V}' \) reduction step)

During the later reduction step the electron in \( \text{V}'' \) occupies one of its the vacant d orbitals. During modification it is important to decide which ([POO\(_{3/2}\)]^0 and
[VOO$_{3/2}$]$^0$) of the structural units modified preferentially. This preference modification has been to dependent on the group electronegativites ($\chi$) of the units (Indeed this has been shown to lead similar results as from a consideration bond energy hierarchies). The unit which has higher $\chi$ value picks up O$^2$ ion and gets modified. The group electronegativites are given in Table 3.1 and have been calculated using the well known Sanderson's method [67] (Sanderson's procedure is briefly described in Appendix-I).

In the glass compositions examined in this work, various structural units are expected to form if ZnO acts as a modifier. These groups are listed in Table 3.1. As seen in Table 3.2, 20 mol% ZnO containing glasses essentially consists of unmodified V$_2$O$_5$ ([VOO$_{3/2}$]$^0$) units. But in 40 mol% ZnO glass there are both [VOO$_{2/2}$O]$^-$ and [VOO$_{3/2}$]$^0$ units which is in accordance with the higher O$^2$ ion activity (higher ZnO concentration) in the glass. It is therefore only in 40 mol% ZnO glass that reactions (3.5B) and (3.6B) have greater possibility of occurring because of higher O$^2$ concentration. This results in greater V$^{4+}$ concentration in the glass and hence higher conductivity. This explains the observed conductivity behavior of the two glasses.

The ZnO may also get incorporated into the network in which case the following scheme of reaction represents the incorporation

$$\text{ZnO} + 2[\text{POO}_{3/2}] \rightarrow [\text{ZnO}_{4/2}]^{2+} + 2[\text{PO}_{4/2}]^{+} \quad (3.7B)$$

Because,

$$\text{P}_2\text{O}_5 = [\text{POO}_{3/2}] \quad \text{and}$$

$$\text{ZnO} = [\text{ZnO}_{2/2}]$$
Table 3.1 Structural groups and their corresponding electronegativities.

<table>
<thead>
<tr>
<th>Groups</th>
<th>Electronegativities</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{POO}_{2/2}]^0)</td>
<td>3.022</td>
</tr>
<tr>
<td>([\text{POO}_{2/2}\text{O}]^-)</td>
<td>2.390</td>
</tr>
<tr>
<td>([\text{POO}_{1/2}\text{O}_2]^{2-})</td>
<td>2.487</td>
</tr>
<tr>
<td>([\text{VOO}_{3/2}]^0)</td>
<td>2.774</td>
</tr>
<tr>
<td>([\text{VOO}_{2/2}]^-)</td>
<td>2.200</td>
</tr>
<tr>
<td>([\text{VOO}_{1/2}\text{O}_2]^{2-})</td>
<td>1.740</td>
</tr>
<tr>
<td>([\text{PO}_{4/2}]^+)</td>
<td>2.074</td>
</tr>
<tr>
<td>([\text{ZnO}_{4/2}]^{2-})</td>
<td>1.009</td>
</tr>
</tbody>
</table>

Table 3.2 Glass composition and expected species when ZnO is in network modifying or network forming positions.

<table>
<thead>
<tr>
<th>Glass Compositions</th>
<th>Network modifying positions</th>
<th>Network forming positions</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO    V_2O_5  P_2O_5</td>
<td>20[POO_{2/2}O]^- 20[POO_{3/2}]^0 140[VOO_{3/2}]^0</td>
<td>([\text{PO}<em>{4/2}]^+ [\text{VO}</em>{4/2}]^-)</td>
</tr>
<tr>
<td>10   70    20</td>
<td>40[POO_{2/2}O]^- 120[VOO_{3/2}]^0</td>
<td>([\text{VO}_{4/2}]^+)</td>
</tr>
<tr>
<td>20   60    20</td>
<td>40[POO_{2/2}O]^- 40[VOO_{2/2}O] 40[VOO_{3/2}]^0</td>
<td>([\text{VO}_{4/2}]^+)</td>
</tr>
<tr>
<td>40   40    20</td>
<td>20[POO_{2/2}O]^- 60[POO_{3/2}]^0 100[VOO_{3/2}]^0</td>
<td>([\text{PO}<em>{4/2}]^+ [\text{VO}</em>{4/2}]^+)</td>
</tr>
<tr>
<td>10   50    40</td>
<td>40[POO_{2/2}O]^- 40[POO_{3/2}]^0 80[VOO_{3/2}]^0</td>
<td>([\text{PO}<em>{4/2}]^+ [\text{VO}</em>{4/2}]^+)</td>
</tr>
<tr>
<td>20   40    40</td>
<td>80[POO_{2/2}O]^- 40[VOO_{3/2}]^0</td>
<td>([\text{VO}_{4/2}]^+)</td>
</tr>
<tr>
<td>40   20    40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
From reaction (3.7B) it is suggested that by the incorporation of ZnO into the network \(\frac{P = O}{P^+ - O^-}\). Here ZnO treated as a network former and is represented as \([\text{ZnO}_{4/2}]^{2-}\) units and Zn presumably is in tetrahedral positions. Similar reaction can occur in \(\text{V}_2\text{O}_5\) or \([\text{VOO}_{3/2}]\) units. Similar incorporation of PbO into networks in glasses have been reported earlier [69,70,74]. The incorporation ZnO therefore requires either \([\text{POO}_{3/2}]^0\) or \([\text{VOO}_{3/2}]^0\) units to be converted \(\frac{\cdot \cdot \cdot}{[\text{POO}_{4/2}]^+}\) or \([\text{VO}_{4/2}]^+\). In Table 3.2 the consequence in terms of structural units present in the glass is also shown. However formation of \([\text{VO}_{4/2}]^+\) by reactions like (3.7B) would suppress the formation of conducting electrons because the envisaged reactions put a far greater demand on available oxygen and no oxygen loss can occur. Also, even if an electron is placed on a \([\text{VO}_{4/2}]^+\) unit it would act as deep trap for the electron and the conductivity can only decrease and not increase. Therefore we prefer to consider incorporation of Zn into network as unlikely.

Another feature of electronic conductivity in this system, which needs to be addressed is that ZnO addition to binary \(\text{V}_2\text{O}_5\)-\(\text{P}_2\text{O}_5\) suppresses conductivity by itself of the latter very dramatically. This is possible only if either V\(^{\text{VII}}\) concentration decreases or the barrier for electron hopping increases.

In the binary glass \([\text{VOO}_{3/2}]^0\) are in the matrix of \([\text{POO}_{3/2}]^0\) (\(\text{P}_2\text{O}_5\)) matrix. Which is generally very reducing environment. Therefore \([\text{VOO}_{3/2}]^0\) is readily reduced at higher temperature to \([\text{VO}_2]^+\) or to \([\text{VO}_{4/2}]^0\) units with attendant loss of oxygen. But this does not result in oxidation of \([\text{POO}_{3/2}]^0\) units since \(\text{O}_2\) is lost in the process. The reductive influence of \([\text{POO}_{3/2}]^0\) units is instigated significantly when it
is converted to \([\text{POO}_{2\alpha}\text{O}]^-\) units making reduction of \([\text{VOO}_{3\gamma}]^\nu\) through loss of oxygen that is much more difficult. This is perhaps the primary reason for the severe reduction in the concentration of \(V^\nu\) in the resulting glasses.

3.4B ACTIVATION ENERGY

Activation energies calculated by linear regression analysis of Arrhenius plots of \(\log (\sigma)\) versus \((1000/T)\). The calculated values of activation energies were found to be lie in the range of 0.2 to 0.7 eV. Figures 3.4 and 3.5 show the variation of activation energy versus mol\% ZnO in LP and HP glass system respectively. In LP glasses, the activation energy decreases with increase of ZnO upto 20 mol\% and then increases with further increase of ZnO. This appears to be consistent with the structural model of these glasses proposed above because of the following considerations. The electronic conductivity barrier is firstly dependent on the distance between the carrier centers; because of the wave function overlap decreases with distance. Secondly, the barrier should decrease with increasing number of carriers for the overlap to increase. Thirdly, barrier should increase if the concentration of oppositely charged ions increase in the structure. It may be seen from the table 3.2 that in LP glasses, the first two compositions have only neutral \([\text{VOO}_{3\gamma}]^0\) groups.

Although in the second composition the number of \([\text{VOO}_{3\gamma}]^0\) groups decrease their effective distances may decrease because of the flexibility of meta-phosphate chains which result in closer packing of \([\text{VOO}_{3\gamma}]^0\) groups, thus the activation energy, \(W\), decreases. But when ZnO content increases further, the concentration of the
Figure 3.4 Variation of activation energy versus ZnO mol% in LP Glasses
Figure 3.5 Variation of activation energy versus ZnO mol% in HP Glasses
resulting $[\text{VOO}_2\text{O}]^-$ itself decreases and so also the effective concentration of potential $[\text{V}^{\text{IV}}\text{OO}_3\text{O}]^-$ centers. Therefore the barrier is found to increase. At still higher ZnO concentration increasing number of carrier electrons and decreasing number of potential $[\text{V}^{\text{IV}}\text{OO}_3\text{O}]^-$ centers cancel each other effect leading to the observed almost constant barrier for conduction.

In the HP glasses, there is a continuous decrease of hopping centers (namely $[\text{V}^{\text{IV}}\text{OO}_3\text{O}]^-$ units) and this appears to dominate the influences on the barriers. Hence almost continuous increase in barrier heights is observed.

### 3.5B INFRARED SPECTROSCOPY

Infrared absorption spectra of various compositions of different series of glasses have been recorded. A small quantity of glass powder was mixed with spectroscopic grade KBr and was palletized using high pressure press. The spectra were recorded at room temperature by using a double beam IR spectrometer (Perkin Elmer 580) in the region of 400 cm$^{-1}$ to 2000 cm$^{-1}$ at room temperature.

#### 3.5B.1 Infrared studies of Zinc-Vanado-Phosphate glasses

The IR spectra recorded in the region of 400 cm$^{-1}$ to 2000 cm$^{-1}$ of LP and HP glasses exhibit composition dependent trends. The recorded spectra of the glasses are shown in figures 3.6 and 3.7. In all glasses significant changes occur in both peak position and intensities. The spectra are generally dominated by features attributable to the phosphate and vanadium unit. The different peak positions and corresponding peak assignments and references are shown in table 3.3.
Fig. 3.6 Infrared spectra of LP glasses
Fig. 3.7 Infrared spectra of HP glasses

(a) 10 ZnO - 40P₂O₅ - 50V₂O₅
(b) 20 ZnO - 40P₂O₅ - 40V₂O₅
(c) 30 ZnO - 40P₂O₅ - 30V₂O₅
(d) 40 ZnO - 40P₂O₅ - 20V₂O₅
(e) 50 ZnO - 40P₂O₅ - 10V₂O₅
Phosphate glasses are composed of PO$_4$ tetrahedra, which consists of long chains or rings of PO$_4$ sharing corners. According to Muller [71] absorption of the P=O group is around 1282-1205 cm$^{-1}$ in many Phosphate glasses. The stretching bands of P-O$^-$ (NBO) are around 1150-1050 cm$^{-1}$. Absorption at 800-720 cm$^{-1}$ is due to P-O-P vibrations (BO). The bands below 600 cm$^{-1}$ are due to the bending mode of the PO$_4$ units. Osaka et al [72] have shown that PO$_4$ unit has two bridging oxygen bonds along with two non-bridging oxygen bonds such as P = O and P - O$^-$. Therefore the infrared spectra are split into two bands with higher energy assigned to the double bonds and lower energy band due to P-O$^-$ bonds [73].

Table 3.3 Infrared absorptions in zinc-vanado-phosphate glasses

<table>
<thead>
<tr>
<th>Peak position</th>
<th>Assignment</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>400-430 cm$^{-1}$</td>
<td>V-O-V bending</td>
<td>79</td>
</tr>
<tr>
<td>430-450 cm$^{-1}$</td>
<td>O-P-O bending</td>
<td>88</td>
</tr>
<tr>
<td>525-675 cm$^{-1}$</td>
<td>V-O-P, O-V-O stretching</td>
<td>77, 79, 87</td>
</tr>
<tr>
<td>700-760 cm$^{-1}$</td>
<td>P-O-P Anti-symmetric</td>
<td>73, 86</td>
</tr>
<tr>
<td>900-996 cm$^{-1}$</td>
<td>V-O stretching, V=O</td>
<td>78, 79, 85</td>
</tr>
<tr>
<td>1000-1100 cm$^{-1}$</td>
<td>PO$_4^3^-$</td>
<td>74, 83, 84</td>
</tr>
<tr>
<td>1150-1250 cm$^{-1}$</td>
<td>P=O</td>
<td>73, 82, 83</td>
</tr>
<tr>
<td>1500-1750 cm$^{-1}$</td>
<td>P-O stretching</td>
<td>69, 81</td>
</tr>
</tbody>
</table>

Rivoalen [76], Anderson [77] and Kulieva [78] have shown that in vanadate glasses the absorption stretching bands of V=O are around 900-1000 cm$^{-1}$. Bands
around 700-710 cm\(^{-1}\) are assigned due to vibrations involving \([\text{VOO}_{3/2}]^0\) groups. The bands around 430-450 cm\(^{-1}\) due to V-O-V bending motions \([79]\). The bands below 400 cm\(^{-1}\) can be assigned due to the bending modes of either PO\(_4\) or VO\(_4\) groups \([80]\).

The nature of V\(_2\)O\(_5\) and P\(_2\)O\(_5\) glass can be considered as built from primary structural units of \([\text{VOO}_{3/2}]^0\) and \([\text{POO}_{3/2}]^0\). When these units are normally connected in the glass three type of linkages namely, P-O-P, V-O-V and P-O-V and \([\text{POO}_{3/2}]^0\) to found at random. Because of the differences in electronegativities, \(\chi\) of the structural units (see table 3.1) heterogroup connectivities formed. In both LP and HP series of glasses show characteristic absorption peaks due to phosphate and vanadium group vibrations. In LP glasses the weak shoulder like peak appearing around 1100 cm\(^{-1}\) for glass containing 10 and 20 mol\% of ZnO is attributed to P=O stretching of \([\text{POO}_{3/2}]^0\) groups. The reported values of P=O vibrations is in the region of 1200-1260 cm\(^{-1}\) \([73]\). In the present glass system due to the added ZnO oxide modifies the \([\text{POO}_{3/2}]^0\) groups which results in weakening of the structure and hence the red shift. This peak vanishes at higher concentration of ZnO while in HP glasses because of high concentration of P\(_2\)O\(_5\) the peak around 1200 cm\(^{-1}\) is consistently present. The peaks around 1050 cm\(^{-1}\) to 1100 cm\(^{-1}\) are attributed to symmetric and asymmetric modes of PO\(_4\) \([74,75]\). These peaks gradually shift towards lower frequencies with increase of ZnO concentration is due to breaking up of P-O-P chains. The absorption peaks around 750 cm\(^{-1}\) are attributable to the bending modes of P-O-P. The peak around 950 cm\(^{-1}\) is due to V=O vibrations which consistently present in both LP and HP series.

V-O-V bending modes seem to overlap at P-O-P bending modes \([76]\) and new peak
occurring around 500 cm\(^{-1}\) can be attributed to the vibrations due to P-O-V linkages [77,79]. The spectra become more complex in the case of glasses with higher percent of ZnO and are probably due to high degree of modification.

3.6B ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY

The EPR experiments were made on powdered glass samples using a Varian E11 spectrometer working in X-band frequency at 9.475 GHz. The modulation amplitude was kept at 100 KHz. All spectra were recorded at room temperature. The modulation amplitude and power levels were maintained at constant values so that neither broadening nor saturation of the signal was observed. Scan range, time constant, field setting, scan time and modulation frequency were all maintained at pre-set values, except receiver gain, which was adjusted to get good derivative signals.

3.6B.1 EPR studies of Zinc-Vanado-Phosphate glasses

Electron paramagnetic resonance (EPR) is a powerful technique based upon resonant absorption of microwaves by unpaired electrons tuned by an external magnetic field. Paramagnetic ions in crystals, organic free radicals, colour centers, irradiation damaged centers etc, are some of the systems for which this technique is employed. Generally in solids, paramagnetic ions are introduced as impurities in the host crystals and the EPR spectrum is studied. The electron of paramagnetic ion shows characteristic behavior, which enables its configuration to be determined by EPR spectrum, for example, valance state, hyperfine interactions with nuclear spins, site symmetry of the paramagnetic ion etc. There are a number of books, which give
detailed account of the above applications and the basic theory of EPR spectroscopy [89-91,93] In the following section we briefly summarizes the basic principles of EPR, and the work carried out by the author on Zinc-Vanado-Phosphate glasses

In EPR spectroscopy, transitions between the Zeeman energy levels of the orbital ground state are observed. The transitions depend upon the particular ion or the paramagnetic center, the symmetry, the strength of the crystal field, spin orbit coupling and hyperfine interaction. These can be well described using a "Spin Hamiltonian" [92,94]

\[ \mathcal{H} = \beta H \mu S + I A S + S D S \]  

(38B)

Here the three terms are the Zeeman interaction, the hyperfine interaction and crystal field interaction.

Generally, for the glass scientist the parameters, which are of interest are the g-values and the hyperfine coupling constants \(A_\parallel\) and \(A_\perp\). The g-value is dimensionless constant, which can be determined experimentally from the EPR spectrum. If the g-values differ from the free spin value (2.0023), it is attributed to the different environment of the paramagnetic ion. For example, if the electric field through which the electron moves is not spherically symmetric then there is a possibility of the orbital angular momentum contributing to the g-value via spin orbit coupling leading to a change in the g-value. An axial environment may give rise to two g-values corresponding to (i) a principal absorption when the external magnetic field is perpendicular to symmetry axis \((g_x = g_y = g_\perp)\) and (ii) a minor absorption when the symmetry axis is parallel \((g_z = g_\parallel)\) to the applied field. Hyperfine coupling
constant is due to the interaction between the electron spin and nuclear spin values.

The EPR spectrum of $d^1$ ions in glass can be described by the following axially symmetric spin Hamiltonian [94.95]

$$H = g_H H z S_z + g_s (H x S_x + H y S_y) + A (I_z S_z + A (I_x S_x + I_y S_y) \quad (3.9B)$$

Where the parallel and perpendicular signs indicate the corresponding components of the parameters. EPR spectrum of $V^{4+}$ is rich in hyperfine structure due to the $^{51}V$ nucleus ($I = 7/2$) and can be easily observed at room temperature.

At the resonance condition, the parallel components of the Hamiltonian in equation (1) are given by

$$H_{||}(m_l) = H_{||}(0) - A_{ll} (m_l^2 / 2H_{||}(0)) [I(I+1)-m_l^2] \quad (3.10B)$$

And the perpendicular components are given by

$$H_{\perp}(m_l) = H_{\perp}(0) - A_{\perp} m_l - (A_{ll}^2 + A_{ll}^2 / 4H_{\perp}(0)) [I(I+1)-m_l^2] \quad (3.11B)$$

Where $H_{||}(0) = h v / g_{||} \beta$, $H_{\perp}(0) = h v / g_{\perp} \beta$, and the other notations have their usual meanings.

The EPR spectra of LP and HP glasses are as shown in figures 3.8 and 3.9.

As described in the previous section the EPR of $^{51}V$ show characteristic hyperfine structure. In LP glasses characteristic hyperfine structure is being observed, although the spectra were not well resolved and therefore the spectral parameters could not be evaluated. The hyperfine structure seen in glasses with $V_2O_5$ upto 30 mol% gradually decreases with further increase of $V_2O_5$ and results in broad spectrum with very weak hyperfine structures. In the case of HP glasses a broad spectrum is observed centered
a) 50 ZnO-20P₂O₅-30V₂O₅
b) 40 ZnO-20P₂O₅-40V₂O₅
c) 20 ZnO-20P₂O₅-60V₂O₅
d) 10 ZnO-20P₂O₅-70V₂O₅

Fig. 3.8 Electron paramagnetic spectra of LP glasses
Fig. 3.9 Electron paramagnetic spectra of HP glasses

- a) $10\text{ZnO} - 40\text{P}_2\text{O}_5 - 50\text{V}_2\text{O}_5$
- b) $20\text{ZnO} - 40\text{P}_2\text{O}_5 - 40\text{V}_2\text{O}_5$
- c) $30\text{ZnO} - 40\text{P}_2\text{O}_5 - 30\text{V}_2\text{O}_5$
- d) $40\text{ZnO} - 40\text{P}_2\text{O}_5 - 20\text{V}_2\text{O}_5$
around \( g = 2 \) and the line width of the signal increases with increase of \( V_2O_5 \) concentration. Figure 3.10 shows the variation of line width versus \( ZnO \) concentration. The absence of hyperfine structure and large line width suggests that in HP glasses there is strong exchange interaction between vanadium ions itself; this interaction is weaker in LP glasses. The calculated values of line width have been tabulated as shown in table 3.4

**Table 3.4 Glass composition and line width (\( \Delta H \))**

<table>
<thead>
<tr>
<th>Glass composition</th>
<th>Linewidth (( \Delta H )) in Gauss</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>V(_2)O(_5)</td>
</tr>
<tr>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>50</td>
<td>10</td>
</tr>
</tbody>
</table>

### 3.7B MAGIC ANGLE SPINNING-NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

MAS-NMR spectroscopy is a powerful tool to study the local environment of a given atomic species in condensed phases. The isotropic NMR chemical shift is very sensitive to the chemical nature of both nearest and the next nearest neighbours [97-100]. A nucleus with non-zero nuclear spin \( (I \neq 0) \) possess a nuclear magnetic
Figure 3.10 Variation of Line width versus ZnO mol% for HP Glasses.
dipole moment $\mu$ and thus the magnetic fields of moments $\mu$ of nuclei in the neighbourhood produce local fields ($H_{\text{local}}$) at the site of the nucleus under observation and is given by relation

$$H_{\text{local}} = \pm \mu/r^3 (3\cos^2\theta - 1)$$

(3.12B)

Where $r$ is the distance between the nuclei and $\theta$ is angle between their binding vector and the external field in $z$-direction. The signs '+' and '-' describe the two possibilities for the neighbour spin orientations to parallel (up) or anti-parallel (down) to the external field. In a solid sample there may exist many such pairs of spins with different $r$ and $\theta$ and therefore, that $H_{\text{local}}$ and the resonance frequency is different for different spins resulting in a broad resonance line. These local fields of the nearest neighbours may be in the order of several gauss and consequently dipolar broadened line widths in the kHz range are to be observed. As already discussed in Chapter 1, to remove broadening interactions the technique of MAS-NMR has been developed. Spinning causes an averaging out of the coordinate dependent quantities. When the sample is spun about an axis which inclined at $54^\circ 44'$ to the external magnetic field, the anisotropic contributions in the terms $H_D$ vanish and because the average value of $3\cos^2(54^\circ 44' - 1)$ is zero. The chemical shift is also reduced to the isotropic value.

3.7B.1 MAS-NMR studies on zinc-vanado-phosphate glasses

$^{31}P$ MAS-NMR spectra were recorded with a Bruker MSL-300 solid state high resolution spectrometer operating at 121.495 MHz (magnetic field 7.05 T). A delay time of 30 $\mu$s was allowed between pulses to ensure relaxation of phosphorous nucleus. Chemical shift values were calculated with respect to $^{31}P$
resonance in 85% H₃PO₄.

The MAS-NMR spectra of the ³¹P nucleus were examined for 10, 20, and 40 mol% of ZnO of both LP and HP glasses and the spectra are shown in figures 3.11 and 3.12. The spectra were recorded at a spinning speed of 7 kHz. All the chemical shifts are identified on the basis of ¹³P in ultra and metaphosphate groups [102] and are listed in table 3.5. The ultra and metaphosphates are designated by NMR studies as Q₃ and Q₂ respectively. Where the subscripts indicate the number of bridging oxygen connected to the phosphorous atom. With the addition of ZnO results in depolymerization of glass network resulting in reduction of the number of cross-linking P-O-P bonds between pairs of tetrahedra and hence the peaks are affected significantly. Pure P₂O₅ is a three dimensional disordered network of PO₄ tetrahedra, most of which are linked at three corners [103].

**Table 3.5 Glass composition and corresponding chemical shift.**

<table>
<thead>
<tr>
<th>Glass composition</th>
<th>Chemical shift in ppm for Q₂</th>
<th>Chemical shift in ppm for Q₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO  V₂O₅  P₂O₅</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10    70    20</td>
<td>-28 13</td>
<td>not resolved</td>
</tr>
<tr>
<td>20    60    20</td>
<td>-16 2</td>
<td>-</td>
</tr>
<tr>
<td>40    40    20</td>
<td>-22 54</td>
<td>-</td>
</tr>
<tr>
<td>10    50    40</td>
<td>-25.6</td>
<td>-31 5</td>
</tr>
<tr>
<td>20    40    40</td>
<td>-16.5</td>
<td>-38 2</td>
</tr>
<tr>
<td>40    20    40</td>
<td>-12.2</td>
<td>-</td>
</tr>
</tbody>
</table>
a) 10 ZnO - 20 P₂O₅ - 70 V₂O₅
b) 20 ZnO - 20 P₂O₅ - 60 V₂O₅
c) 40 ZnO - 20 P₂O₅ - 40 V₂O₅

Fig. 3.11 P³¹ MAS-NMR spectra of LP glasses
Fig. 3.12 $^{31}$P MAS-NMR spectra of HP glasses

a) $10\text{ZnO}-40\text{P}_2\text{O}_5-50\text{V}_2\text{O}_5$

b) $20\text{ZnO}-40\text{P}_2\text{O}_5-40\text{V}_2\text{O}_5$

c) $40\text{ZnO}-40\text{P}_2\text{O}_5-20\text{V}_2\text{O}_5$
We assume that all the ZnO are only acting as glass modifiers in both LP and HP glass composition region. The scheme of modification with the addition of ZnO takes place according to the group electronegativities on different phosphate and vanadate groups as already described in section 3.3B. Consequence of modification is clearly seen in the MAS-NMR spectra of both LP and HP series. Glass with 10 mol% of ZnO contains both [POO$_{3/2}$]$^0$ and [POO$_{2/2}$O]$^-$ groups. Therefore, the MAS-NMR spectrum shows a broad signal due to the presence of these two species. With increase of ZnO a well defined sharp peak is seen indicating only one type of species i.e [POO$_{2/2}$O]$^-$ and its corresponding chemical shift -22.54. In HP glasses the MAS-NMR spectrum is similar to that of LP glasses except the intensities are higher, this is expected since these glasses have high concentration of phosphate.

CONCLUSIONS

We have carried out the dc conductivity, IR, EPR, and MAS-NMR studies on ZnO-V$_2$O$_5$-P$_2$O$_5$ glasses. Conductivity of both LP and HP glass systems have been carried out over a temperature range of 360-520 K. DC Conductivity of these glasses indicates that the conductivity is through small polaronic hopping. Significant changes in the plots of conductivity against composition were observed at different concentration of ZnO. Results have been discussed in light of the modifications of glass structure. Results based on the various structural groups present in these glasses indicate that ZnO behaves as modifier. IR studies of both series of glasses show the characteristic absorption peaks due to phosphate and vanadium vibrations and show composition dependent trends. EPR of $^{51}$V show the characteristic hyperfine
structure only in LP glasses while in HP glasses the spectra are not well resolved due to strong exchange interaction of vanadium ion. $^{31}$P MAS-NMR studies have been carried to ascertain the presence of different phosphate species. In LP series of glass with 10 mol% ZnO the MAS-NMR spectra show broad resonance attributable to phosphorous in $\text{[POO}_2\text{O]}^-$ and $\text{[POO}_3\text{O]}^-$ groups. With increase of ZnO concentration results into a single type of species, $\text{[POO}_2\text{O]}^-$ which is seen in MAS-NMR spectra. In HP glasses also a similar trend is seen but the intensities of the signals are higher than those compare to LP glasses.
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