Influence of WO₃ on dielectric properties of zinc phosphate glasses

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Received 19 March 2001; accepted 4 July 2001

Dielectric constant $\varepsilon'$, loss tan $\delta$ and a.c conductivity $\sigma_{ac}$ of 40 ZnO-xWO₃ (60-x) P₂O₅ (with 0 ≤ x ≤ 15) glasses are studied as a function of frequency (in the range $10^2$-$10^5$ Hz) and temperature (range 30-300°C). The dielectric breakdown strengths of these glasses are also measured in the air medium. All the dielectric parameters (viz., $\varepsilon'$, tan $\delta$ and $\sigma_{ac}$) are found to decrease with the increase in the concentration of WO₃. Dielectric loss variation with the temperature for the glasses containing WO₃ up to 5 mol% exhibited dipolar relaxation effects. These effects are analysed by a pseudo Cole-Cole plot method. The dielectric breakdown strength, the activation energy for a.c conduction are found to decrease with increase in concentration of WO₃. These results have been used to throw some light on the structural change in ZnO-WO₃-P₂O₅ glass system with the aid of data on IR spectra and differential thermal analysis of these glasses.

The study of dielectric properties, such as dielectric constant $\varepsilon'$, loss tan $\delta$ and a.c conductivity $\sigma_{ac}$ over a wide range of frequency and temperature and also the dielectric breakdown strength of the glasses helps in assessing their insulating character; these studies may also help in understanding the structure of the glass to some extent. Work along these lines was carried out in recent years on a variety of inorganic glasses by a number of researchers yielding valuable information.

P₂O₅ glasses have several advantages over conventional silicate and borate glasses due to their superior physical properties such as high thermal expansion coefficients, low melting and softening temperatures and high ultra-violet transmission. However, the poor chemical durability, high hygroscopic and volatile nature of phosphate glasses prevented them from replacing the conventional glasses in a wide range of technological applications. In recent years, there has been an enormous amount of research on improving the physical properties and the chemical durability of phosphate glasses by introducing a number of glass formers and modifiers such as Al₂O₃, MoO₃, Cr₂O₃, Ta₂O₅, Sb₂O₅, As₂O₅ etc., into P₂O₅ glass network.

Among various phosphate glass systems, zinc phosphate glasses are considered as interesting glasses, zinc oxide has the ability to get into phosphate network in both metaphosphate and pyrophosphate glasses forming ZnO₄ tetrahedra which link adjacent phosphate chains together through bridging oxygens. The transition metal ions such as tungsten, dissolved in ZnO-P₂O₅ glass matrix influence the insulating character of these glasses very strongly because tungsten oxide participates in the glass network forming, with different structural units like WO₄ and WO₆. Further, it is expected that, tungsten oxide groups form a single tungsten – phosphorus – oxygen framework with the phosphorus tetrahedrons, strengthen its structure and raises the chemical resistance of the glass. Most of the studies available on phosphate glasses are on optical (such as Raman spectra, IR spectra, optical absorption, luminescence etc.,) and elastic properties, though few studies on electrical properties (mostly on d.c. conductivity especially of some binary systems like CdO-P₂O₅, PbO-P₂O₅ etc.,) of some phosphate glasses exists in literature, much devoted studies particularly on dielectric properties such as dielectric relaxation, a.c. conductivity and breakdown strength of ZnO-WO₃-P₂O₅ system are not available.

The aim of the present investigation is to have a comprehensive understanding of the influence of tungsten ions on the insulating character of zinc phosphate glasses from a systematic study on dielectric constant $\varepsilon'$, loss tan $\delta$, a.c conductivity $\sigma_{ac}$ of ZnO-WO₃-P₂O₅ glasses in the frequency range $10^2$-$10^5$ Hz and temperature range of room temperature to 300°C and also the dielectric breakdown strength in air medium. Further in this study, it is intended to throw some light on the structural modifications (with the help of IR spectral studies and differential thermal
Experimental Procedure

Five 40 ZnO-xWO_3-(60-x)P_2O_5 glasses with x=0, 3, 5, 10 and 15 were synthesized. These compositions are referred to as glasses A, B, C, D and E. Glass with 20 mol% WO_3 did not form.

Appropriate amounts (all mol %) of Analar grade reagents of ZnO, WO_3 and P_2O_5 were thoroughly mixed in an agate mortar and melted in a platinum crucible (tungsten free glass, glass A, at 840°C and the rest of the glasses between 950 and 1050°C in a PID temperature controlled furnace for about \( \frac{1}{2} \) h until a bubble free liquid was formed. The resultant melt was then cast in a brass mould and subsequently annealed at about 300°C. Transparent light blue glasses were obtained. It may be noticed here that when the concentration of WO_3 is increased beyond 15% the glasses became opaque with thick blue colour and crystalline nature was observed. The amorphous nature of the glasses was confirmed by X-ray diffractograms recorded on Seifert Diffractometer Model SO DEBYE FLUX-2002 instrument. The samples were then ground and finely polished. The final dimensions of the samples used for the present measurements were about 1 cm \( \times \) 1 cm \( \times \) 0.2 cm. The density \( (d) \) of the glasses was determined to an accuracy of 0.001 following Archimedes' principle using xylene (99.99% pure) as the medium of flotation. A thin coating of silver paint was applied (to the larger area faces) on either side of the glasses to serve as electrodes for dielectric measurements. The dielectric measurements were made on LCR Meter (Hewlett-Packard Model-4263B) in the frequency range 10^2-10^5 Hz. Dielectric breakdown strength for all the glasses was determined at room temperature in air medium using a high a.c. voltage breakdown tester (ITL Model AAH-55, Hyderabad) operated with an input voltage of 250 V at a frequency of 50 Hz; it was ensured that all the glasses used for this study were of almost identical thickness. Infrared transmission spectra of these glasses was recorded using a FT/IR-5300 Fourier Transform infrared spectrophotometer (Jasco make) in the frequency range 400-4000 cm\(^{-1}\) by KBr pellet method. The glass transition temperature \( (T_g) \), the crystallisation temperature \( (T_c) \) and melting temperature \( (T_m) \) were measured using Seiko TG/DTA 32 balance, at a heating rate of 20°C/min.

Results

From the measured values of the density \( (d) \) and calculated average molecular weight \( (M) \), various physical parameters such as W\(^{6+}\) ion concentration \( N_t \), mean W\(^{6+}\) ion separation distance \( (R_p) \) and the field strength \( (F_p) \), which are useful for understanding dielectric properties of these glasses are evaluated using standard formulae \(^{22}\) and presented in Table 1. This table also contains the values of glass transition temperature evaluated from DTA traces.

Fig. 1a presents the differential thermal analysis traces of the glasses under investigation. It is observed that the glass transition temperature \( (T_g) \) increases as the concentration of WO_3 increases (Table 1). Further, an exothermic peak \( (T_e) \) due to the crystallisation followed by another endothermic peak due to the remelting of the glass \( (T_m) \) are also observed for these glasses. The variations in the parameters \( T_g/T_m, (T_e-T_g)/T_g, (T_e-T_m)/T_m \) and \( K_g= (T_e-T_g)/(T_m-T_e) \), (which gives the information of the glass forming ability) with WO_3 concentration are presented in Fig.1b; these values are found to increase with increase in the concentration of WO_3.

<table>
<thead>
<tr>
<th>Property</th>
<th>Glass A (x = 0)</th>
<th>Glass B (x = 3)</th>
<th>Glass C (x = 5)</th>
<th>Glass D (x = 10)</th>
<th>Glass E (x = 15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density ( (d) ) ( (g/cm^3) )</td>
<td>2.749</td>
<td>2.918</td>
<td>3.011</td>
<td>3.162</td>
<td>3.311</td>
</tr>
<tr>
<td>Average molecular weight ( (M) )</td>
<td>117.71</td>
<td>120.41</td>
<td>122.21</td>
<td>126.71</td>
<td>131.20</td>
</tr>
<tr>
<td>W(^{6+}) ion concentration ( N_t )</td>
<td>--</td>
<td>4.38</td>
<td>7.42</td>
<td>15.03</td>
<td>22.38</td>
</tr>
<tr>
<td>Inter-ionic distance of W(^{6+}) ions ( (R_p) ) ( (nm) )</td>
<td>--</td>
<td>1.32</td>
<td>1.10</td>
<td>0.87</td>
<td>0.76</td>
</tr>
<tr>
<td>Polaron radius ( (R_p) ) ( (nm) )</td>
<td>--</td>
<td>0.53</td>
<td>0.45</td>
<td>0.35</td>
<td>0.31</td>
</tr>
<tr>
<td>Field strength ( (F_p) ) ( (10^3 \text{ cm}^{-2}) )</td>
<td>--</td>
<td>2.13</td>
<td>3.03</td>
<td>4.85</td>
<td>6.40</td>
</tr>
<tr>
<td>Breakdown Strength ( (B) ) ( (kV/cm) )</td>
<td>16.0</td>
<td>22.1</td>
<td>22.3</td>
<td>22.7</td>
<td>23.1</td>
</tr>
<tr>
<td>Glass Transition temperature ( (T_g) ) ( (°C) )</td>
<td>449</td>
<td>475</td>
<td>503</td>
<td>523</td>
<td>547</td>
</tr>
</tbody>
</table>

Table 1—Various physical properties of 40 ZnO-xWO_3-(60-x)P_2O_5 glasses
The variation of dielectric constant $\varepsilon'$ and loss tan $\delta$ at room temperature ($30^\circ$C) of ZnO-P$_2$O$_5$ glasses with concentration of WO$_3$ is represented in Fig. 2. With the introduction of WO$_3$, the values of dielectric constant and loss are found to decrease gradually with increase in the concentration of WO$_3$; further for any particular concentration of WO$_3$, the values of $\varepsilon'$ and tan $\delta$ are found to decrease considerably with increase in frequency (Fig. 2).

The temperature dependence of $\varepsilon'$ at different frequencies for glass B (containing 3% WO$_3$) is shown in Fig. 3a and for different concentrations of WO$_3$ at 1 kHz is in Fig. 3b; $\varepsilon'$ is found to exhibit
considerable increase at higher temperatures. This increase is more pronounced at lower frequencies; in addition it is also observed that the value of $\varepsilon'$ (at fixed temperature and frequency) decreases with increase in the concentration of WO$_3$.

The variation of dielectric loss $\tan \delta$ with temperature at different frequencies of glass B (containing 3% of WO$_3$) is shown in Fig. 4a; these curves have distinct maxima, with increase in the frequency, the temperature maximum of $\tan \delta$ shifts towards higher temperatures and with increase in the temperature, the frequency maximum shifts towards higher frequencies, indicating the relaxation character of dielectric losses in these glasses.

The effect of WO$_3$ concentration on the relaxation strength of these glasses can be clearly understood from Fig. 4b where $\tan \delta$ at 10 kHz is plotted against temperature for different concentrations of WO$_3$; the glass A, which is free from WO$_3$, has exhibited a relaxation peak with the highest value of $(\tan \delta)_{\text{max}}$. With successive increase in the concentration of WO$_3$, the temperature region of relaxation shifted towards higher temperatures with decreasing values of $(\tan \delta)_{\text{max}}$; further, it seems, there has been an absence of such relaxation effects for the glasses containing high concentration of WO$_3$ (> 5%).

Using the relationship:

$$f = f_0 \exp \left(-\frac{W_d}{kT}\right),$$  \hspace{1cm} (1)

where $f$=frequency, $f_0$=constant.

the effective activation energy $W_d$ for the dipoles is calculated for these glasses and is presented in Table 2 along with the other pertinent data. The activation energy $W_d$ is found to increase with increase in WO$_3$ content.

The a.c. conductivity $\sigma_{\text{ac}}$ is calculated at different temperatures using the equation:

$$\sigma_{\text{ac}} = \omega e_0 \varepsilon' \tan \delta,$$  \hspace{1cm} (2)

$\omega = 2\pi f$, where $f$=frequency and $e_0$ is the vacuum dielectric constant for different frequencies and plots of log $\sigma_{\text{ac}}$ against $1/T$ are shown in Fig 5a for glass C containing 5% of WO$_3$ and for all the glasses at 100 kHz in Fig. 5b. From these plots the activation energy for the conduction in the high temperature

<table>
<thead>
<tr>
<th>Glass</th>
<th>$(\tan \delta)_{\text{max}}$ at 100 kHz</th>
<th>Temp. region of relaxation (°C)</th>
<th>Activation energy for dipoles (eV)</th>
<th>Spreading factor $\beta$ (rads)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (0% WO$_3$)</td>
<td>0.342</td>
<td>52-95</td>
<td>1.08</td>
<td>0.51</td>
</tr>
<tr>
<td>B (3% WO$_3$)</td>
<td>0.200</td>
<td>60-100</td>
<td>1.21</td>
<td>0.44</td>
</tr>
<tr>
<td>C (5% WO$_3$)</td>
<td>0.096</td>
<td>65-103</td>
<td>1.31</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Fig. 4a—Variation of dielectric loss with temperature for ZnO-P$_2$O$_5$ glass containing 3% WO$_3$ for different frequencies (glass B).

Fig. 4b—Comparison plot of variation of dielectric constant with the temperature of ZnO-WO$_3$-P$_2$O$_5$ glass at 10 kHz.
region over which a near linear dependence of log \( \sigma_{ac} \) with \( 1/T \) could be observed is evaluated and presented in Table 3; this activation energy is found to be the lowest for glass A (WO\(_3\) free glass) and found to increase with increase in the concentration of WO\(_3\) (Table 3).

The dielectric breakdown strength for the glass A is determined to be 16 kV/cm; the values of breakdown strengths are found to increase from glass A to E (Table 1).

**Discussion**

Zinc phosphate glasses containing tungsten oxide have a complex composition and are an admixture of network formers, intermediates and modifiers. P\(_2\)O\(_5\) is a well-known network former with PO\(_4\) structural units with one of the four oxygen atoms in PO\(_4\) tetrahedron is doubly bonded to the phosphorus atom\(^{18}\).

The PO\(_4\) tetrahedrons are linked together with covalent bonding in chains or rings by bridging oxygens. Neighbouring phosphate chains are linked together by cross-bonding between the metal cation and two non-bridging oxygen atoms of each PO\(_4\) tetrahedron\(^{29}\). In general, the P-O-P bond between PO\(_4\) tetrahedra is much stronger than the cross bond between chains via the metal cations\(^{29}\). WO\(_3\) belongs to the intermediate class of glass forming oxides; it is an incipient glass network former and as such does not readily form the glass but does so in the presence of the modifier oxides like ZnO with WO\(_4\) and WO\(_6\) structural units\(^{17}\). The WO\(_4\) tetrahedra may enter the glass network and alternate with PO\(_4\) tetrahedra. ZnO is in general a glass modifier and enters the glass network by breaking-up the P-O-P bonds (normally the oxygens of ZnO break the local symmetry while Zn\(^{2+}\) ions occupy interstitial positions) and introduces co-ordinated defects known as dangling bonds along with non-bridging oxygen ions; in this case Zn\(^{2+}\) is octahedrally co-ordinated. However, ZnO may also participate in the glass network with ZnO\(_4\) structural units when zinc is linked to four oxygens in a covalency bond configuration. Further, when ZnO is present in larger quantities, the \( \pi \)-bond of P=O may be ruptured with the creation of new non-bridging oxygen ions facilitating the formation of P-O-Zn linkages\(^{11}\).
The presence of different structural groups in these glasses can be verified from the IR spectra Fig. 6. The IR spectra of ZnO-WO₃-P₂O₅ glasses recorded at room temperature have exhibited three groups of absorption bands due to different structural units of WO₃, ZnO and P₂O₅. (i) Bands due to WO₃: two clearly resolved bands due to WO₄ groups, one in between 415 and 435 cm⁻¹ (identified due to v₄ vibrations of WO₄ groups, the presence of vibrational bands due to ZnWO₄ group may also not be ruled out in this range) and the other prominent band between 920 and 950 cm⁻¹ (due to deformed WO₄ polyhedra or more precisely due to v₁(A₁) type vibrations) are present in these glasses; with increase in the concentration of WO₃, the band due to v₄ vibrations is observed to be shifted gradually towards higher wavenumber from 418 (glass B) to 435 cm⁻¹ (glass E) with decreasing intensity. The band due to deformed WO₄ polyhedra is also observed to be shifted towards higher wavenumber with decreasing intensities indicating a transformation of WO₄ to WO₆ groups. In general, WO₆ groups are more strongly interconnected into three dimensional units than WO₄ groups since these WO₆ groups share more than one bridging oxygen ion and the position of these polyhedra in the glass network will be in such a way so as to decrease the long range disorder. Obviously, the bands due to these groups are not present in glass A; (ii) bands due to ZnO: a band due to ZnO₄ units has been observed between 500 and 560 cm⁻¹ (ref. 30), with increase in the concentration of WO₃ this band is found to be shifted towards higher wavenumber with descending intensity indicating the decrease in the concentration of ZnO₄ units and giving the scope for cross-linking of Zn-O-W; (iii) bands due to P₂O₅: three groups of bands due to phosphoryl structural units have been observed (a) in the region 1250-1270 cm⁻¹ due to P=O stretchings (this region may also consist of bands due to antisymmetrical vibrations of PO₂⁻ groups), the wavenumber of this band is found to be shifted towards higher values with decreasing intensities from 1252 cm⁻¹ (glass A) to 1269 cm⁻¹ (glass E) with increase in the content of WO₃, (b) in the region 1000-1100 cm⁻¹, which may be assigned to the vibrations of PO₃⁻ and PO₄⁻ structural groups and (c) another group of bands between 700-760 cm⁻¹ due to P-O-P vibrations. The summary of data on positions of various IR spectral bands, observed in the ZnO-WO₃-P₂O₅ glasses is presented in Table 4.

Table 4—Summary on positions (cm⁻¹) of various absorption bands in the IR spectra of ZnO-WO₃-P₂O₅ glasses.

<table>
<thead>
<tr>
<th>Structural groups</th>
<th>Glass A</th>
<th>Glass B</th>
<th>Glass C</th>
<th>Glass D</th>
<th>Glass E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tungsten groups WO₄(v₄)</td>
<td>—</td>
<td>418</td>
<td>420</td>
<td>427</td>
<td>435</td>
</tr>
<tr>
<td>WO₄(v₁(A₁))/WO₆</td>
<td>—</td>
<td>923</td>
<td>927</td>
<td>936</td>
<td>945</td>
</tr>
<tr>
<td>Zinc groups ZnO₄</td>
<td>525</td>
<td>530</td>
<td>533</td>
<td>538</td>
<td>544</td>
</tr>
<tr>
<td>Phosphoryl groups P-O-P</td>
<td>725</td>
<td>730</td>
<td>734</td>
<td>745</td>
<td>750</td>
</tr>
<tr>
<td>PO₄³⁻ , PO₃⁻</td>
<td>1005</td>
<td>1020</td>
<td>1045</td>
<td>1065</td>
<td>1085</td>
</tr>
<tr>
<td>P=O and PO₂⁻</td>
<td>1252</td>
<td>1257</td>
<td>1261</td>
<td>1265</td>
<td>1269</td>
</tr>
</tbody>
</table>

Among various polarizations (viz., electronic, ionic, orientational and space charge) the space charge polarization depends on the purity and perfection of the glasses. The considerably higher values of dielectric constant and loss of ZnO-WO₃-P₂O₅ glasses at room temperature (Fig. 2), observed at low frequencies, may be ascribed to the bonding defects produced in the glass lattice which contribute to the space charge polarization. The large increase in the values of ε' and tan δ (beyond relaxation region) with temperature can also be attributed to space charge polarization since other contributions for dielectric constant like electronic and orientation polarizations do not increase with temperature.

With successive increase in WO₃ concentration from 0 to 15% the values of ε', tan δ and σₑ are found to decrease at any temperature and frequency; such a
decrease may be ascribed due to the following reasons: (i) there is a possibility for the cross-linking of a part of ZnO units with WO₄ units to form Zn-O-W bonds in the glass network; this is reasonable because of close ionic radii of W⁶⁺ (0.74 Å) and Zn²⁺ (0.74 Å) (from CRC Handbook-CRC Press, Florida). A similar linkage between phosphorus and tungsten ions (P-O-W) as mentioned before is also possible because the ionic radius of P⁵⁺ (0.42 Å) is also nearer to that of W⁶⁺ ion. The more structural units of tungsten enter the glass framework, higher are such type of linkages, the stronger is the glass network; (ii) the decrease in the dielectric parameters with successive increase in WO₃ concentration (from glass B to E) can also be understood due to the transformation of WO₄ to WO₆ units (evidence from IR spectra). These WO₆ groups are in general be more strongly interconnected (due to stoichiometric reasons) into three dimensional units than WO₄ groups which obviously lessen the disorderliness in the glass network.

Yet another reason for decrease of these dielectric parameters with increasing concentration of WO₃ (from glass A to E), may also be given from IR spectra in which the band due to antisymmetrical vibrations of PO₄ groups (which is included in the high wavenumber side of P=O vibrational region) is shifted towards higher wavenumber with decreasing intensities, indicating increasing symmetry of the glass network.

Tan δ versus temperature curves for zinc phosphate glasses, show dipolar relaxation effects with decreasing relaxation character with increasing concentration of WO₃ and probably there seems to be absence of these relaxation effects when WO₃ is present beyond 5%. To know whether there is single relaxation time or spreading of relaxation times in ZnO-WO₃-P₂O₅ glasses, we have adopted a pseudo Cole-Cole plot method (instead of conventional Cole-Cole plot between ε'(ω) and ε''(ω) at a fixed temperature) suggested by Sixou in which ε'(T) is plotted against ε''(T) at a fixed frequency. This indicates the spreading of relaxation times, which means several types of dipoles are present in these glasses.

Further, the nature of variation of ε'(T) and tan δ, with temperature for these glasses indicates that the Cole-Davidson equation:

$$\varepsilon'(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + i\omega\tau}.$$  \hspace{1cm} (3)

(where $T$ is temperature, $\varepsilon_{\infty}$ is low temperature dielectric constant, $\varepsilon_s$ is high temperature dielectric constant and $\tau$ relaxation time) can safely be applied to these glasses. Separating real and imaginary terms of above equation gives expressions for $\varepsilon'$ and $\varepsilon''$. The plot between $\varepsilon'(T)$ and $\varepsilon''(T)$ known as pseudo Cole-Cole cuts $\varepsilon'$ axis at low temperature side at an angle of $(\pi/2)\beta$, where $\beta$ is the spreading factor for relaxation times. Fig. 7 shows a pseudo Cole-Cole plot for glass B at 1 kHz. The spreading factor $\beta$ estimated from this plot is 0.44. Such plots have also been drawn for glasses A and C and the value of $\beta$ is estimated in a similar way; the value of $\beta$ is found to decrease with increase in the concentration of WO₃ (Table 2). Though it may not be possible from the present measurements to identify an unique mechanism responsible for dielectric relaxation (observed in the glasses A, B and C), it seems reasonable to attribute these effects due to association of octahedrally positioned Zn²⁺ ion with a pair of PO₄ groups (which exhibit the vibrational bands in the high frequency side of P=O vibrational region as mentioned earlier) in analogy with the mechanism-association of a divalent positive ion with a pair of cationic vacancies in conventional glasses, glass ceramics and crystals in which the relaxation effects are observed. The non-zero values of $\beta$ obtained for these glasses indicate the dipoles experience an approximately random potential energy on diffusing through the distorted structure of the glass.

It is interesting to find that the nature of variation of $\varepsilon'$ and tan δ with temperature is similar. The variation of $\varepsilon'$ with temperature can be connected to frequency through modified Debye equation as

![Fig. 7 — A pseudo cole-cole plot for glass B at 1 kHz.](image)
reported earlier\textsuperscript{33,34}. A plot of log ($\Delta e'$) against $1/T$ (where $\Delta e'$ is the difference between dielectric constant at any temperature $T$ and that at room temperature) at different frequencies for (glass D) is shown in Fig. 8; the graphs obtained are straight lines having about the same slope for all the frequencies in the high temperature region. The computed activation energy is 0.44 eV. This value is practically the same as the activation energy for a.c. conduction in the same temperature region in these glasses. This seems to suggest that the charge carriers responsible for change in $e'$ and $\sigma_{ac}$ with temperature in this temperature range are the same. A similar analysis was also carried out on the other glasses and found to yield the similar result (Table 3).

In general, the a.c. conductivity of the amorphous material where charge carriers experience an approximately random potential energy on diffusing, is found to obey the equation \textsuperscript{41}:

$$\sigma(\omega)=A\omega^s$$

with $s<1$ (up to the frequency of 1 MHz), is considered to signify the coupling of an ion's movement with its environment\textsuperscript{41,42}. Though various models have been developed to interpret the a.c. conduction mechanism in the glasses, we have attempted to explain a.c. conduction in the present ZnO-WO$_3$-P$_2$O$_5$ glasses on the basis of quantum mechanical tunnelling (QMT) model.

The equation for a.c. conductivity due to quantum mechanical tunnelling is given by\textsuperscript{41}:

$$\sigma(\omega)=\eta e^2 kT [N(E_F)]^{1/2} \alpha^{-5} \omega^4 \left[ \frac{\ln \frac{v_{ph}}{\omega}}{\omega} \right]^4,$$  \hspace{1cm} (5)

where $N(E_F)$ is the density of the energy states near the Fermi level, $\alpha$ is the electronic wavefunction decay constant, $v_{ph}$ is the phonon frequency and $\eta$ is a constant and its value is given by $\eta=\pi/3$ (Austin & Mott\textsuperscript{41}), $=3.66\pi^2/6$ (Butcher & Hyden\textsuperscript{43}), $=\pi^4/96$ (Polak\textsuperscript{44}).

The plot of log $\sigma(\omega)$ versus log $\omega$ for glass C at a temperature of 318 K is shown in Fig. 9. The graph obtained is a straight line. Plots drawn for the other glasses have also yielded the straight lines. The experimental values of $s$ obtained for these glasses are presented in Table 3 along with the other important data on a.c. conduction.

Among various mechanisms of conduction in the amorphous materials (such as band conduction, conduction in extended states, conduction in localised states near the band edge and conduction in the localised states near the Fermi level), the conduction in the localized states near the Fermi level occurs when a.c. conductivity is nearly temperature independent and varies linearly with frequency. The conduction in present ZnO-WO$_3$-P$_2$O$_5$ glasses in the low temperature region (up to 318 K) can safely be attributed to take place by this mechanism. The value of $N(E_F)$, i.e., the density of energy states near Fermi level, for a frequency of $10^4$ Hz and at 318 K, $\alpha$ is evaluated from the plot of log $\sigma_{ac}$ against $R_t$ and $v_{ph} = 5 \times 10^{12}$ Hz, is computed using Eq. (5), with the value of numerical constant $\eta$ suggested by different investigators and presented in Table 3. The value of $N(E_F)$ is found to decrease from glass B to E. Further
more, the range of \( N(E_F) \) values obtained \( =10^{19} \) eV\(^{-1}\)cm\(^3\); such values of \( N(E_F) \) suggest the localized states near the Fermi level\(^{42}\). The increase in the activation energy (Table 3) for a.c. conduction in ZnO-WO\(_3\)-P\(_2\)O\(_5\) glasses with increase in WO\(_3\) concentration (from glass B to E) obviously indicates the decrease in the density of these energy states.

When the dielectric is placed in an electric field, the heat of dielectric loss is liberated. If the applied field is an alternating field, the specific dielectric loss, i.e., the loss per unit volume of the dielectric is given by:\(^{46}\)

\[
\rho_l = \varepsilon_0 \varepsilon' \tan \delta \frac{B}{6} \ 	ext{W/m}^3.
\]  

(6)

This equation indicates that smaller the values of \( \varepsilon' \tan \delta \) of the glass at a given frequency, the lower are the losses. In a dielectric across which the voltage is applied, heat is liberated, the temperature of the field is an alternating field, the specific dielectric loss, i.e., the loss per unit volume of the dielectric is given by Eq. (6).

Our observations on breakdown strengths of ZnO-WO\(_3\)-P\(_2\)O\(_5\) glasses, as mentioned earlier, indicate that the rate of increase of \( \varepsilon' \tan \delta \) with temperature is the highest for glass A and lowest for glass E. Though the breakdown strengths are actually determined at room temperature, the heat liberated during the breakdown, raises the temperature of the glass and hence raises the \( \varepsilon' \tan \delta \) value. Since, the rate of increase of \( \varepsilon' \tan \delta \) with temperature is the highest for glass A, the breakdown strength is the lowest when compared with that of other glasses. Thus, the experiments on the dielectric breakdown strength of ZnO-WO\(_3\)-P\(_2\)O\(_5\) glasses reveal that there is a decrease in the disorderliness with increase in the concentration of WO\(_3\). A similar conclusion can be drawn from the data on DTA. The increase in the parameters \( T_d/T_m \) (\( T_d/T_m = (T_\text{c}-T_\text{g})/T_\text{m} \) and \( K_{gl} = (T_\text{c}-T_\text{g})/(T_\text{m}-T_\text{g}) \) with WO\(_3\) concentration indicate the increase in the rigidity of the glass network.

Conclusions

The study of dielectric properties of ZnO-WO\(_3\)-P\(_2\)O\(_5\) glasses in combination with IR spectra and differential thermal analysis seems to be an useful tool for understanding the structure of these glasses to a considerable extent. The detailed studies on dielectric properties such as \( \varepsilon' \), \( \tan \delta \) and \( \sigma_m \), and their variation with frequency and temperature and also the dielectric breakdown strength indicate that the gradual increase in the introduction of WO\(_3\) (up to 15 mol\%) into zinc phosphate glasses causes a substantial increase in the stability of glass network.

Acknowledgements

One of the authors (P S) wishes to thank University Grants Commission New Delhi for awarding teacher fellowship under F.I.P scheme. She also expresses her gratefulness to Dr. Sr. Marietta Pudota, Principal St. Theresa’s College for Women, Eluru for granting study leave. The authors also thank Prof. G R Desaraju, Dean, School of Chemistry, University of Hyderabad, Hyderabad, for kindly extending the facility to record IR spectra of the glasses used in this investigation.

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