Spectroscopic investigation of tungsten ions in
\[ \text{PbO–Sc}_2\text{O}_3–\text{P}_2\text{O}_5 \] glass matrix

\[ \text{PbO–Sc}_2\text{O}_3–\text{P}_2\text{O}_5 \] glass containing different concentrations of \( \text{WO}_3 \) ranging from 0 to 5 mol\% were prepared. A number of studies, viz. differential thermal analysis (DTA), infrared spectra, optical absorption and Electron Spin Resonance (ESR) spectra have been carried out. The results of DTA indicated the highest glass forming ability for the glass containing 5 mol\% of \( \text{WO}_3 \). The results of spectroscopic studies have been analyzed in the light of different oxidation states of tungsten ions.
Spectroscopic investigation of tungsten ions in PbO–Sc$_2$O$_3$–P$_2$O$_5$ glass matrix

5.1 Introduction

Oxide glasses are cheap and can be synthesized easily in a wide range of compositions. The most common glasses are formed by mixing glass formers like silicon dioxide (SiO$_2$), borate (B$_2$O$_3$), and phosphate (P$_2$O$_5$) with metal oxides like lead oxide (PbO) as modifiers. The oxygen in the metal oxide plays an important role in the glass matrix to create higher disorder in the glass. Since it is necessary to know how the coordination of the glass former varies when combines with modifier, and how the modifier oxygens are bonded with different ligands, the structural characterization of the glass with creative network formation becomes a demanding task [1].

Phosphate glasses are declared as laser hosts and solid state ionic conductors [2]. Phosphate glasses have been proved their candidature for some glass to metal sealing applications, because of their low glass transition temperatures and high thermal expansion coefficients compared to silicate glasses. Recently, phosphate glasses have received a great deal of attention due to their potential application in optical data transmission, detection, sensing and laser technology, biocompatibility waveguide and fiber optical amplifier devices [3–6]. Lead oxide has the ability to form stable glasses over a wide range of concentrations due to its dual role as a glass modifier and as a glass former [7]. These glasses may also be of particular interest for the non-linear optical effects, similar to other PbO complex glasses doped with rare earth ions.
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. Among the high-index materials, Scandium oxide (Sc$_2$O$_3$) is a promising material in the ultraviolet ~UV spectral range for laser optical coatings, due to its relatively high damage threshold [11–16]. The property of phototropism of WO$_3$ mixed glasses, they are proposed as promising candidates for application in information display devices of high memory [17, 18]. WO$_3$ containing host materials are also widely used in smart windows to control solar input of buildings or related to large area displays [19, 20]. The tungsten ions doped in silicate glasses influence the physical properties of the glasses to a large extent because the these ions exist in different valence states viz., W$^{6+}$, W$^{5+}$ and W$^{4+}$. It is shown by the following thermo reversible disproportionate reaction in spite of the original oxidation state of the ion in the starting glass batch [21–23].

\[
W^{5+} + W^{5+} \leftrightarrow W^{4+} + W^{6+}
\] (5.1)

W$^{6+}$ ion participates in the glass network with different structural units like WO$_4$ (T$_d$) and WO$_6$ (O$_h$) where as W$^{5+}$ ions form the complexes of the type W$^{5+}$O$_3^-$ and occupy octahedral positions. During recent studies on WO$_3$ containing glass networks like phosphate, borate, silicate etc., it is indicated that with the increment of WO$_3$ results a progressive breaking of the tetrahedral linkages of the host glass network [24–26].

The objective of this paper is to have a comprehensive understanding over the topology and valence states of tungsten ions in PbO–Sc$_2$O$_3$–P$_2$O$_5$ glass
system, by a systematic study of ESR spectra coupled with spectroscopic investigations (optical absorption and IR spectra). Such studies will definitely be useful for widen the scope for practical utility of these glasses.

The detailed compositions of the glasses used in the present study are as follows:

\[
\begin{align*}
    W_0: & \quad 40\text{PbO–10Sc}_2\text{O}_3–50\text{P}_2\text{O}_5 \\
    W_1: & \quad 40\text{PbO–9 Sc}_2\text{O}_3–50\text{P}_2\text{O}_5: 1\text{WO}_3 \\
    W_2: & \quad 40\text{PbO–8 Sc}_2\text{O}_3–50\text{P}_2\text{O}_5: 2\text{WO}_3 \\
    W_3: & \quad 40\text{PbO–7 Sc}_2\text{O}_3–50\text{P}_2\text{O}_5: 3\text{WO}_3 \\
    W_4: & \quad 40\text{PbO–6 Sc}_2\text{O}_3–50\text{P}_2\text{O}_5: 4\text{WO}_3 \\
    W_5: & \quad 40\text{PbO–5 Sc}_2\text{O}_3–50\text{P}_2\text{O}_5: 5\text{WO}_3
\end{align*}
\]

5.2. Brief review of previous work on WO\textsubscript{3} doped glasses.

P. Srinivasa Rao et al [27] prepared tungsten oxide doped ZnF\textsubscript{2}–Bi\textsubscript{2}O\textsubscript{3}–P\textsubscript{2}O\textsubscript{5} glass-ceramics and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS) and differential thermal analysis (DTA) techniques. Thomas Scheike et al [28] studied Luminescence in WO\textsubscript{3}–P\textsubscript{2}O\textsubscript{5}–ZnO glasses. A blue emission by 320 nm excitation was observed, Raman spectroscopy on the glasses showed the presence of WO\textsubscript{6} groups in the glass. Shaaban M. Salem et al [29] studied Dielectric properties, conductivity, UV–visible and infrared spectroscopy of PbO-P\textsubscript{2}O\textsubscript{5}-NaF glasses containing WO\textsubscript{3}. The short range structures of the phosphate samples were examined by Fourier transform infrared spectroscopy. Bozena Burtan et al [30] Multi component telluride-tungstate glasses
containing Nd$^{3+}$ and Er$^{3+}$ ions at 77 and 293 K using spectroscopic methods. The Judd–Ofelt intensity parameters were derived from the absorption spectra and used to calculate the radiative lifetimes and branching ratios. H.A. ElBatal et al [31] studied Optical and FT infrared spectral properties of tungsten ions in a host lead borate glass with composition PbO 55%, B$_2$O$_3$ 45% (wt%) were studied. The same spectral properties were re-measured after subjecting the samples to successive gamma irradiation. Optical studies of WO$_3$-doped sample indicate the presence of tungsten ions mostly in the hexavalent W$^{6+}$ state. N. SrinivasaRao et al [32] have been studied Lead bismuth arsenate glasses mixed with different concentrations of WO$_3$ (ranging from 0 to 6.0 mol%). Differential thermalanalysis (DTA), opticalabsorption, ESR and IR spectral studies have been carried out. Gurinder PalSingh et al [33] prepared Glass $x$Al$_2$O$_3$–20PbO–(80–$x$) B$_2$O$_3$ and $x$WO$_3$–$x$Al$_2$O$_3$–20PbO–(80–2$x$)B$_2$O$_3$ with $x$ varying from 0% to 10% mole. The optical band gap decreases (from 3.21 to 2.37 eV) more for WO$_3$–Al$_2$O$_3$–PbO–B$_2$O$_3$ glasses with an addition of WO$_3$ content. The FTIR spectral studies have pointed out the conversion of structural units of BO$_3$ to BO$_4$ andWO$_4$ to WO$_6$ in these glasses.

Gurinder PalSingh et al [34] prepared Pure and WO$_3$ doped CeO$_2$–PbO–B$_2$O$_3$ glasses. The structural and optical analyses of glasses are carried out by XRD, FTIR, density and UV–v is spectroscopic measurement techniques. Ch. Srinivasa Rao et al [35] synthesized Li$_2$O–ZrO$_2$–SiO$_2$: Pr$_2$O$_3$/Er$_2$O$_3$ mixed with three interesting sesquioxides (viz., Al$_2$O$_3$, Sc$_2$O$_3$, Y$_2$O$_3$) glasses. Optical absorption and fluorescence spectra were studied the Judd–Ofelt theory was
applied to characterize the absorption and luminescence spectra of Pr$^{3+}$ and Er$^{3+}$ ions in these glasses. A. Mohan Babu et al [36] studied the effect of concentration on photoluminescence properties of Sm$^{3+}$ ions doped lead tungstate tellurite (LTTSm) glasses by using the absorption, emission and decay measurements. Ch. Srinivasa Rao et al [37] synthesized a series of Li$_2$O–Al$_2$O$_3$–ZrO$_2$–SiO$_2$ glasses doped with different concentrations of WO$_3$ (0 to 5.0 mol%). Differential thermal analysis of the samples indicated increasing glass forming ability with the increasing concentration of WO$_3$ in the glass matrix. A variety of spectroscopic (optical absorption, IR, Raman and ESR) and dielectric properties (over a range of frequency and temperature) of these glasses have been investigated.

Roger Gomes Fernandes et al [38] investigated Pb (PO$_3$)$_2$–WO$_3$–PbF$_2$ and doped with Er$^{3+}$ in order to prepare luminescent transparent glass-ceramics. Thermal properties such as thermal stability and crystallization behavior upon heating were investigated by DSC in function of PbF$_2$ content. F.H. ElBatal et al [39] studied ultraviolet–visible and infrared spectroscopic techniques to investigate the undoped lithium phosphate glass and other samples of the same composition doped with varying WO$_3$ contents. The same spectroscopic properties were measured after subjecting the samples to 3 and 6 Mrad doses of gamma irradiation on the measured properties. F.H. ElBatal et al [40] studied tungsten-doped sodium phosphate glasses of various compositions and with varying WO$_3$ contents were prepared. UV–visible and infrared spectroscopic studies were measured before and after successive
gamma irradiation. Raman and ESR studies were conducted for some selected glass samples. Y. Gandhi et al [41] synthesized the glasses of the composition \((45-x)\text{ZnF}_2-x\text{WO}_3-49\text{TeO}_2:1.0\text{Nd}_2\text{O}_3/\text{Sm}_2\text{O}_3/\text{Eu}_2\text{O}_3\) with \(x\) varying from 5 to 20 mol\% Optical absorption, fluorescence spectra (in the spectral range 400–2300 nm) and also fluorescence decay were studied at ambient temperature. The Judd–Ofelt theory analysis was applied to characterize the absorption and luminescence spectra of \(\text{Ln}^{3+}\) ions in these glasses. Y. Gandhi et al [42] prepared and characterized three series of glasses, of the composition 20 MO (\(M = \text{Ca, Pb, Zn}\))–40 Sb\(_2\)O\(_3\)–(40–\(x\)) B\(_2\)O\(_3\):\(x\)WO\(_3\), with six values of \(x\) ranging from 0 to 1 mol\%. The samples were characterized by X-ray diffraction, scanning electron microscopy, EDS and differential scanning calorimetric techniques. The variations observed in all these properties due to different modifiers as a function of the concentration of WO\(_3\) have been analyzed in the light of different oxidation states and environment of tungsten ions in these glasses.

D. Munoz-Martín et al [43] Characterized as potential candidates for photonic devices, non-linear materials and coatings, 22 glasses in the TeO\(_2\)–WO\(_3\)–PbO system. Structural characterisation of the glasses was conducted through FTIR spectrometry and UV–VIS spectra were recorded to determine optical absorption/transmission and energy gap values. DTA curves yielded data of transition temperature (\(T_g\)), onset crystallisation temperature (\(T_c\)) and the thermal stability range of glasses. Fatma Hatem ElBatal et al [44] Investigated undoped lead phosphate glass of the composition PbO 50 mol\%,
P$_2$O$_5$ 50 mol% together with samples of the same ratio doped with various WO$_3$ contents. UV–Visible spectroscopic studies were measured before and after successive gamma irradiation. K. Sambasiva Rao et al [45] prepared Li$_2$O–WO$_3$–P$_2$O$_5$ glasses containing small concentrations of Ag$_2$O from 0 to 1 mol%. A number of studies viz., chemical durability, dielectric studies, spectroscopic (infrared, optical absorption ESR spectra) and magnetic susceptibility studies of these glasses, have been carried out. Hesham Afifia et al [46] prepared 20WO$_3$–(80–x) TeO$_2$–xPbO ternary tellurite glasses (x = 10, 12.5, 15, 17.5 and 20 mol%) The longitudinal ultrasonic attenuation measurements are studied using pulse echo method at fundamental frequencies of 2, 4, 6 and 8MHz. The internal friction, acoustic activation energy, deformation potential, relaxation strength, number of loss centers and density of state have been

O. Cozar et al [47] have characterized xWO$_3$·(100-x)[2P$_2$O$_5$·PbO] and xMoO$_3$·(100-x)[2P$_2$O$_5$·PbO] glass systems with 0≤x≤50 mol% by IR, Raman and EPR spectroscopy. G. Little Flower et al [48] studied PbO–Sb$_2$O$_3$–As$_2$O$_3$ glass containing different concentrations of WO$_3$ ranging from 0 to 2 mol%. A number of studies, viz., differential thermal analysis (DTA), magnetic susceptibility, infrared spectra, optical absorption and ESR spectra have been carried out. P. Subbalakshmi et al [49] prepared Tungsten phosphate glasses mixed with the three different modifier oxides, viz., PbO, ZnO and CaO doped with Er$_2$O$_3$ were prepared. The glasses were characterised by X-ray diffraction spectra, electron microscopy and differential thermal analysis. Optical absorption and photoluminescence spectra of these glasses have been studied.
Marcelo Nalin et al [50] studied glass formation in the ternary system InF$_3$–BaF$_2$–[Sc (PO$_3$)$_3$]$_n$. Glasses were characterized by Differential Scanning Calorimetry, vibrational spectroscopy (Raman) and $^{31}$P NMR. Sindhu et al [51] studied and reported that the WO$_3$ has exhibited interesting optical property like electrochromism, which has important applications in gas sensor, optical smart window and display devices. Churbanov et al [52] reported that the glasses of TeO$_2$–WO$_3$ (TWO), TeO$_2$–WO$_3$–La$_2$O$_3$ (TWLO) and some other systems may be considered as perspective materials for fiber optics. Gael Poirier et al [53] have studied the local order around the tungsten ions in tungstate fluorophosphate glasses by X-ray absorption spectroscopy. Poirier and Poulain et al [54] have reported the increase of characteristic temperatures, density and refractive index as tungsten oxide content increases. Lim et al [55] have reported the detailed investigations on the structure of some alkali tungsten tellurite glasses by means of X-ray photoelectron spectroscopy. Nunzi Conti et al [56] have reported the characterization of ion-exchanged wave guides in tungsten tellurite and zinc tellurite Er$^{3+}$ doped glasses. Cenk et al [57] and Ozen et al [58] Adding a low quantity of WO$_3$ improves luminescence, a fact which has been confirmed by optical measurements in TeO$_2$–WO$_3$–Tm$_2$O$_3$ systems.

Boudlich et al [59] reported that the presence of W$^{5+}$ ions confers to the glasses colors that change with composition. Srinivasa Rao and Veeraiah [60] have reported the detailed investigations on the influence of tungsten ions on some physical properties of arsenate glasses. These authors [61] have also
studied nonlinear absorption measurements on fluorophosphate glasses with high concentrations of tungsten oxide. Murugan and Varma et al [62] have studied the characterization of lithium borate-bismuth tungstate glasses and glass ceramics by impedance spectroscopy. Ovcharenko and Smirnova et al [63] have presented the glass formation areas, crystallization ability, optical parameters and physical properties of B$_2$O$_3$–WO$_3$–B$_2$O$_3$ systems. Rakhimov et al [64] have reported the EPR study of W$^{5+}$ pairs in lithium tungsten phosphate glasses. In their study they have reported that the tungsten ions exist in the glass in W$^{4+}$, W$^{5+}$ and W$^{6+}$ states. Hager et al [65] have reported the infrared and Raman spectra of tungsten oxyfluoride glasses and assigned the observed absorption bands to different vibrational modes. This study has shown that the structural units formed in these glasses include WO$_4$ tetrahedral and WO$_6$ octahedral groups. Bhagat et al [66] have reported the optical and electrical properties of binary WO$_3$–Pb$_3$O$_4$ glasses. Chowdari and Kumari et al [67] have prepared Ag$_2$O–WO$_3$–TeO$_2$ glasses and have characterized them by X-ray diffraction, differential scanning calorimetry, X-ray photoelectron spectroscopy (XPS), Raman and Fourier transform-infrared (FT-IR) spectroscopy and electrical conductivity studies. El-Desoky et al [68] have studied physical properties of alkali borate tungsten glasses and concluded that the increase in the electrical conduction was due to hopping mechanism between two sites of tungsten viz., W$^{5+}$ and W$^{6+}$.

Weinberg et al [69] reported that the tungsten ion exists in different valence states W$^{6+}$, W$^{5+}$, W$^{4+}$, etc. hence its doping can affect the structure and
optical properties of host glasses. Selvaraj et al [70] have reported physical, thermal and spectroscopic properties, such as density, molar volume, micro-hardness, heat capacity, glass transition temperature and infrared spectral changes in K₂O–WO₃–P₂O₅ glasses and proposed a structural model to rationalize the experimental observations. Selvaraj et al [71] reported that the ability of tungsten to have several oxidation states opens possibilities for electro-optical applications. Leland et al [72] studied the oxide glasses doped with transition metal oxides such as WO₃ and V₂O₅, which are reported to exhibit semiconducting properties and hence these glasses have been extensively studied from the electronics point of view. Koffyberg and Benko et al [73] have investigated conductivity and optical absorption of zinc borate glasses mixed with 80 % of WO₃; they have analyzed the results using small polaron hopping theory. Miroshnichenko and Mombelli [74] have studied the infrared absorption spectra and the structure of glasses in the WO₃–P₂O₅–Na₂O system over the whole glass forming region and showed that the glass network consists of distorted WO₄ tetrahedra to WO₆ octahedra and the absorption bands in the IR spectra have been assigned to vibrations of the end bands W=O, and W-O-, and of the bridges W–O–W.

5.3 characteraction

5.3.1 XRD

Our visual examination of the samples, absence of peaks in the X-Ray diffraction clearly suggest that the samples prepared are of amorphous in nature.
5.3.2 Physical Parameters

The physical parameters such as tungsten ion concentration $N_i$ and mean tungsten ion separation $r_i$, molar volume ($V_M$) of these glasses are evaluated from the measured values of density $d$ and calculated average molecular weight $\overline{M}$, using the conventional formulae and are presented in Table 5.1.

Table 5.1

Physical parameters of PbO–Sc$_2$O$_3$–P$_2$O$_5$: WO$_3$ glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>Density $d$ (g/cm$^3$) $\pm 0.001$</th>
<th>Average molecular weight, $\overline{M}$ (g/mol) $\pm 0.001$</th>
<th>Conc. of tungsten ions, $N_i$ ($10^{22}$/cm$^3$) $\pm 0.001$</th>
<th>Interionic distance $R_i$ (Å) $\pm 0.00001$</th>
<th>Polaron radius $R_p$ (Å) $\pm 0.00001$</th>
<th>Field strength $F_i$ ($10^{16}$, cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_0$</td>
<td>5.393</td>
<td>174.01</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>$W_1$</td>
<td>5.453</td>
<td>175.94</td>
<td>1.866</td>
<td>3.769</td>
<td>1.518</td>
<td>2.601</td>
</tr>
<tr>
<td>$W_2$</td>
<td>5.513</td>
<td>177.85</td>
<td>3.734</td>
<td>8.926</td>
<td>1.2055</td>
<td>4.128</td>
</tr>
<tr>
<td>$W_3$</td>
<td>5.569</td>
<td>179.61</td>
<td>5.602</td>
<td>5.949</td>
<td>1.053</td>
<td>5.411</td>
</tr>
<tr>
<td>$W_4$</td>
<td>5.621</td>
<td>181.24</td>
<td>7.472</td>
<td>4.461</td>
<td>0.956</td>
<td>6.556</td>
</tr>
<tr>
<td>$W_5$</td>
<td>5.674</td>
<td>182.87</td>
<td>8.343</td>
<td>3.567</td>
<td>0.888</td>
<td>7.609</td>
</tr>
</tbody>
</table>
5.3.3 Differential thermal analysis (DTA) studies

In the Fig. 5.1 scans for PbO–Sc$_2$O$_3$–P$_2$O$_5$ glasses doped with different concentrations WO$_3$ are presented; all the traces exhibited typical glass transition with the inflection point between 397 and 421°C, with the growing content of WO$_3$ in the glass matrix (inset of Fig. 5.1). In the region, 782–820°C, an exothermic peak due to crystallization is observed in the traces of all the glasses. The value of (T$_c$–T$_g$), a parameter that represents thermal stability of a glass against devitrification is found to increase with the content of WO$_3$ in the glass matrix (inset of Fig. 5.1). The values of T$_g$, and T$_c$ obtained for all the glasses are furnished in Table 5.2.

Table 5.2
Summary on data of DTA studies of PbO–Sc$_2$O$_3$–P$_2$O$_5$: WO$_3$ glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>T$_g$ (°C) (±1°C)</th>
<th>T$_c$ (°C) (±1°C)</th>
<th>T$_c$–T$_g$ (°C) (±1°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W$_0$</td>
<td>397</td>
<td>782</td>
<td>385</td>
</tr>
<tr>
<td>W$_1$</td>
<td>390</td>
<td>770</td>
<td>380</td>
</tr>
<tr>
<td>W$_2$</td>
<td>397</td>
<td>780</td>
<td>383</td>
</tr>
<tr>
<td>W$_3$</td>
<td>400</td>
<td>785</td>
<td>385</td>
</tr>
<tr>
<td>W$_4$</td>
<td>412</td>
<td>802</td>
<td>390</td>
</tr>
<tr>
<td>W$_5$</td>
<td>421</td>
<td>820</td>
<td>399</td>
</tr>
</tbody>
</table>
Fig. 5.1 DTA traces of PbO–Sc₂O₃–P₂O₅: WO₃ glasses. Inset shows the variation of $T_g$ and $T_c - T_g$ with the concentration of WO₃.
5.4 Results

5.4.1 Optical absorption spectra

Fig. 5.2(a) presents optical absorption spectra of PbO–Sc₂O₃–P₂O₅: WO₃ glass samples recorded at room temperature in the wavelength range 300–1000 nm. The absorption edge for the glass W₅ is positioned at 336 nm where as for the glass W₁ it is observed at 390 nm.

Additionally, the spectrum of glass W₁ exhibited a broad absorption band centered at about 874 nm. As the concentration of WO₃ is increased, the intensity of these bands is observed to decrease with a slight shift in the peak position towards lower wavelength. The extraction of the data on optical absorption spectra of these glasses is presented in Table 5.3.

From the observed absorption edges, we have evaluated the optical band gaps (Eₒ) of these samples by drawing Urbach plots (Fig. 5.2(b)) between \((\alpha \hbar \omega)^{1/2}\) and \(\hbar \omega\) as per the equation.

\[
\alpha (\omega) \hbar \omega = C (\hbar \omega - E₀)^2
\]  

(5.2)

Higher value of c represents high optical band gap. From the extrapolation of the linear portions of the curves of Fig. 5.2(b). The value of optical band gap (Eₒ) (the intercept on the x- axis) are determined and are presented in Table 5.3.
Table 5.3
Data on optical absorption spectra of PbO–Sc$_2$O$_3$–P$_2$O$_5$: WO$_3$ glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>Cut-off wavelength (nm)</th>
<th>Optical Band gap (eV)</th>
<th>Band position (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_0$</td>
<td>362</td>
<td>3.34</td>
<td>-----</td>
</tr>
<tr>
<td>$W_1$</td>
<td>390</td>
<td>3.06</td>
<td>874</td>
</tr>
<tr>
<td>$W_2$</td>
<td>383</td>
<td>3.16</td>
<td>870</td>
</tr>
<tr>
<td>$W_3$</td>
<td>375</td>
<td>3.20</td>
<td>862</td>
</tr>
<tr>
<td>$W_4$</td>
<td>348</td>
<td>3.42</td>
<td>857</td>
</tr>
<tr>
<td>$W_5$</td>
<td>336</td>
<td>3.48</td>
<td>840</td>
</tr>
</tbody>
</table>

Fig. 5.2(a) Optical absorption spectra of PbO–Sc$_2$O$_3$–P$_2$O$_5$: WO$_3$ glasses.
Fig 5.2(b) Tauc plot of Optical absorption spectra of PbO–Sc$_2$O$_3$–P$_2$O$_5$:WO$_3$ glasses.
5.4.2 ESR spectra

ESR spectra of PbO–Sc₂O₃–P₂O₅ glasses doped with different concentrations of WO₃ recorded at room temperature are shown in Fig. 5.3. The spectra of the glasses exhibited an asymmetric signal (identified due to distorted octahedral W⁵⁺ ions [75] at \( g_\perp = 1.73 \) and \( g_\parallel = 1.62 \); the spectra also exhibited another conventional signal due to paramagnetic O⁻ ion defects at about \( g_\perp = 1.97 \) [75]. As the concentration of WO₃ is increased, a slight decay in the intensity of this signal with increase in the concentration of WO₃ is observed; however the values of g tensors remain unaffected. It may be further noted here that the spectra of the glasses free of WO₃ do not exhibit any significant signal indicating the signal exhibited by doped glasses is due to the tungsten ions.
Fig. 5.3 ESR spectra of PbO-Sc$_2$O$_3$-P$_2$O$_5$ glasses doped with different concentrations of WO$_3$.
5.4.3 IR spectra

Fig. 5.4 shows the effect of WO$_3$ on the infrared spectra of the PbO–Sc$_2$O$_3$–P$_2$O$_5$ glasses. The infrared spectra of the studied glasses showed some different frequency regions. The characteristic IR bands in the present glass systems are furnished in Table 5.4. The bands located at around 1301–1324 cm$^{-1}$ are assigned to the bending vibrations of PO$^{2-}$ groups [76]. These bands may be overlapped with a band assigned to the vibration of PbO$_6$ structural units [77]. The last units have a modifier role. The bands at around 790-803 cm$^{-1}$ are assigned to symmetric stretching vibrations of P–O–P rings [78]. The spectra of the glasses containing WO$_3$, have exhibited three additional bands due to $\nu_1$-WO$_4$, $\nu_4$-WO$_4$ and $\nu_1$-WO$_6$ vibrations at about 942 cm$^{-1}$, 432 cm$^{-1}$ and 987 cm$^{-1}$ respectively [79–82]. The bands at around 878 cm$^{-1}$ are related to P–O–P asymmetric stretching vibrations of bridging oxygen atoms in P–O–P bands. The band at around 1039 cm$^{-1}$ which is attributed to vibrations of PO$_4^{3-}$ groups.

With the gradual incremental introduction of WO$_3$, the following changes have been observed in the spectra: (i) a progressive increase in the intensity of the bands due to symmetrical stretching vibrations of P–O–P and PO$_4^{3-}$ groups and PbO$_4$ structural units and WO$_4$ groups accompanied by a shift towards slightly lower wave number, (ii) the bands due to asymmetric vibrations of phosphate groups and also WO$_6$ groups are shifted towards higher wave number with a considerable decrease in the intensity.
Data on infrared spectra of PbO–Sc₂O₃–P₂O₅: WO₃ glasses recorded at room temperature (Assignment of band positions in cm⁻¹).

<table>
<thead>
<tr>
<th>Glass</th>
<th>PO²⁻ asym.</th>
<th>PO₄³⁻ groups</th>
<th>ν₁ − WO₆</th>
<th>ν₁ − WO₄</th>
<th>P-O-P Asymmetric stretching</th>
<th>P-O-P Symmetric stretching</th>
<th>PbO₄ Units</th>
<th>ν₄ − WO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>W₁</td>
<td>1301</td>
<td>1039</td>
<td>987</td>
<td>942</td>
<td>878</td>
<td>803</td>
<td>474</td>
<td>432</td>
</tr>
<tr>
<td>W₂</td>
<td>1307</td>
<td>1036</td>
<td>983</td>
<td>937</td>
<td>882</td>
<td>801</td>
<td>471</td>
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(b) $\text{PO}_4^{3-}$ groups
(c) $v_1$ - $\text{WO}_6$
(d) $v_1$ - $\text{WO}_4$
(e) P-O-P asymmetric stretching

(f) P-O-P symmetric stretching
(g) PbO$_4$ Units
(h) $v_4$ - $\text{WO}_4$

Fig. 5.4 IR of PbO-$\text{Sc}_2\text{O}_3$-$\text{P}_2\text{O}_5$-$\text{WO}_3$ glasses at room temperature
5.5 Discussion

The polaron radius is decreasing and field strength is increasing on increasing tungsten ion concentration from 1 mol % to 5 mol %. The glass transition temperature ($T_g$) is described as the change in temperature in which a reversible transition occurs in amorphous materials from a hard and relatively brittle state to a molten or rubber-like state. An amorphous material below its $T_g$ (glassy state) behaves like a brittle solid but without a crystalline structure and only has short-range order [83]. It is the temperature at which glass physical properties change.

As the temperature increases, an amorphous solid will become less viscous. At some point the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature ($T_c$). This transition from amorphous solid to crystalline solid is an exothermic process.

The DTA traces of these glasses demonstrate an endothermic effect due to the glass transition temperature $T_g$ between 397 and 421°C, the glass transitions temperature is observed to increase with the increasing content of WO$_3$ in the glass matrix. This is due to the decrement in the non-bridging oxygens (NBO). In the region, 782–820°C, an exothermic peak due to crystallization is observed in the traces of all the glasses. With the enhancement in the content of WO$_3$ in the glass matrix the value of ($T_c$–$T_g$), a parameter that represents thermal stability of a glass against devitrification, is found to increase. The increase in the augmented cross-link density of various structural
groups and the reduction in the closeness of packing are accountable for the increase of these parameters in these glasses. These results manifest that, with the increase in the concentration of WO$_3$ in the glass matrix, tungsten ions regularly occupy network forming positions, increase the cross-link density and enhance the mean bond strength.

Therefore, a decrease in concentration of the NBO ions results in a enhancement of the band gap energy. This is also confirmed by increase in the value of $T_g$ with the increment of WO$_3$ content [84].

The broad band observed in the optical absorption spectra of Lead Scandium Phosphate glasses doped with tungsten ions are recognized due to $d_{xy}$→$d_{x^2-y^2}$ transition of W$^{5+}$ ions. In detail, two optical excitations were predicted starting from $d_{xy}$ ground state, possibly due to strong inter valence charge transfer transition between W$^{5+}$ and W$^{6+}$ ions, the two bands could not be resolved. For glass W$_5$ the intensity and half width of this band observed to be low in the spectrum suggests that the concentration of W$^{5+}$ ions is fairly low in this glass. Thus, the study on optical absorption spectra of Lead Scandium Phosphate glasses doped with tungsten ions confirms the presence of W$^{5+}$ ions in all the glasses. Further, these studies also indicate the presence of the highest concentration of W$^{5+}$ ions in the glass W$_1$. Such W$^{5+}$ ions may form W$^{5+}$O$_3$ molecular orbital states and are expected to participate in the depolymerisation of glass network. Higher the concentration of W$^{5+}$O$_3$ modifiers, higher is the concentration of non-bridging oxygens (NBO) in the glass network. Sc$_2$O$_3$ is a modifier and WO$_3$ a former, considering the metal-oxygen bond strength. The
decrease of $T_g$ from 0 to 1mol % WO$_3$ and the increase for higher concentration may also be related to the presence of W$^{5+}$O$_3^-$ groups which act as modifiers. This leads to an increase in the degree of localization of the electrons there by increasing the donor centers in the glass network. The presence of larger concentration of these donor centers lowers the optical band gap and shifts the absorption edge towards higher wavelength side.

The appearance of asymmetric signal in the ESR spectra of these glasses indicates the behavior of W$^{5+}$ ions is similar to of nd$^1$ ions (with a local C$_{4v}$ symmetry) in oxide glasses. The values of $g_\perp = 1.73$ and $g_\parallel = 1.62$ point out that W$^{5+}$ ions there in axially distorted octahedral positions with a short W–O bond and an opposite long W–O bond along the symmetry axis of oxygen ions [85]. The slight decay in the intensity of the signal with the increase in concentration of the WO$_3$ glass matrix suggests the declining proportions of paramagnetic W$^{5+}$ ions in the glass network. The variations in the ESR line-shape and the intensity in the other glass systems have been previously explained by a number of investigators on the basis of variations in the concentration of paramagnetic spices like W$^{5+}$ ions [86–88]. The line width has to be increased as WO$_3$ molar content grows [89]. The near invariance of the difference between $g_\perp$ and $g_\parallel$ (anisotropy factor) with the concentration of WO$_3$ in the glass network indicates that the structural modifications experienced by W$^{5+}$ octahedron are nominal. Moreover, in these glass samples, the jumping frequency of the charge carriers (W$^{5+}$→W$^{6+}$) is proportional to exp ($-W/kT$), where $W = 1/2W_D+W_H$; in this, $W_D$ is the mean disorder energy difference
between adjacent tungsten sites in the glass network and $W_H$ is the activation energy for the hopping process of the polarons between two identical sites. In the case of samples containing higher content of $WO_3$, it is possible to suppose that the terms $W_D$, and that the jumping rate of the polaron are low; this fact, together with the relatively low concentration of the paramagnetic species accounts for the weak ESR signal observed in the spectra of glasses containing higher concentration of $WO_3$.

In the IR spectra of Lead Scandium Phosphate glasses doped with different concentrations of $WO_3$, as the concentration of $WO_3$ is increased all the symmetrical bands and also bands due to $v_1$-$WO_4$, $v_4$-$WO_4$ is observed to grow at the expense of asymmetrical bands and $WO_6$ octahedral units. This observation conform that in the glass $W_1$, more number of tungsten ions exist in $W^{5+}$ state that act as modifiers and enhance the degree of disorder in the glass network by creating more and more dangling bonds. And observed increasing intensity trend of symmetrical bands in the remaining samples containing $WO_3$ suggests a decreasing concentration of dangling bonds representing activity of tungsten ions in frame-work of four-fold coordination by way of making connection with the two additional oxygen’s through dative bond.

5.6 Conclusions

PbO–$Sc_2O_3$–$P_2O_5$ glasses mixed with different concentrations of $WO_3$ (ranging from 0 to 5.0 mol %) were synthesized. A variety of properties viz.,
Physical, DTA and spectroscopic properties that include optical absorption, ESR and IR have also been investigated.

1. The differential thermal analysis of these samples has indicated increase glass forming ability with increase in the concentration of $\text{WO}_3$.

2. IR spectral study indicate that there is decrease in degree of deformation in the glass network with increase in concentration of $\text{WO}_3$ in the glass matrix; further these studies also specify the possibility of tungsten ions in network forming positions with $\text{WO}_4$ structural units at higher concentration of $\text{WO}_3$.

3. The Optical absorption measurements on all the glasses suggest the reduction of $\text{W}^{6+}$ ions in to $\text{W}^{5+}$ ions with higher percentage in glass $W_1$.

4. The ESR spectral study indicate tungsten ions exists in $\text{W}^{5+}$ state with octahedral environment in large concentrations in glass $W_1$, the studies also recommend relatively higher covalent character for glass $W_5$.

The scrutiny of array of experimental results have point out that Lead Scandium Phosphate glasses doped with low concentration of $\text{WO}_3$ are improved candidates for exhibiting photochromism in view of the fact that they contain higher proportions of $\text{W}^{5+}$ ions. So large proportion of $\text{WO}_3$ is preferable for making Lead Scandium Phosphate glasses doped with $\text{WO}_3$ glasses as good thermal and electrical resistant.
References


