Spectroscopic and EPR studies on PbO–Y$_2$O$_3$–P$_2$O$_5$ glasses doped with Molybdenum ion

The structure of 40PbO–(10–$x$) Y$_2$O$_3$–50P$_2$O$_5$ : $x$ MoO$_3$ glass system with 0 ≤ $x$ ≤ 5 mol% was prepared and investigated by IR, differential thermal analysis techniques, optical absorption and EPR spectroscopy. The characteristic IR bands of these glasses due to the stretching and bending vibrations were identified and analyzed by increasing of MoO$_3$ content. The results of differential scanning calorimetric studies suggest that the glass forming ability is higher for the glasses containing MoO$_3$ beyond 5 mol%. The intensity and frequency variations for the characteristic phosphate group vibrations have been correlated with the changes of the structural units present in these glasses. All the investigated samples exhibit EPR signals which suggest that the molybdenum ions exist in Mo$^{5+}$ state with Mo$^{6+}$ act as modifiers with MoO$_4$ and MoO$_6$ structural groups in these glasses. The shapes of spectra are also changed with the increasing of molybdenum ions content.
Spectroscopic and EPR studies on PbO–Y₂O₃–P₂O₅ glasses doped with Molybdenum ion

3.1 Introduction

Phosphate glasses, despite of their poor chemical durability have many biomedical and technological applications. Phosphate materials containing calcium oxide are intensely studied because they may have bioactive potential. Such materials with calcium oxide can be produced to have similar bone structure or to be used as microstructures for active implant. On the other hand phosphate materials containing lead oxide are used in the nuclear technique as nuclear waste encapsulation. Phosphate based glasses are both scientifically and technologically important materials because they generally offer some unique physical properties better than other glasses because of the linked PO₄ structural units with covalent bonding in chains or rings by bridging oxygen’s [1–4]. These glasses have poor chemical durability that often limits their usefulness that can be improved by the substitution of various oxides such as lead oxide [5, 6] have low melting and glass transition temperature [7, 8] high electrical conductivity[9] high thermal expansion coefficient [10] and high ultraviolet transmission [11, 12]. These properties making them useful candidates for fast ion conducting materials [13] laser host matrices after doping with rare-earth elements [14, 15] glass-to-metal seals [16] and for the immobilization and disposal of nuclear waste were reported [17, 18]. Investigations of lead phosphate glasses have revealed that the modifier/former role of PbO depends on PbO concentration in the glass
composition 40 PbO–(10–x)Y$_2$O$_3$–50P$_2$O$_5$–x MoO$_3$ with 0 ≤ x ≤ 5 mol%. The created P–O–Pb bonds along with the high ionic field strength and polarizability of Pb$^{2+}$ ions control the physical properties of lead phosphate glasses. Depending on the studied glass system, the Pb$^{2+}$ ions show an intermediate character between former and modifier. As a glass former PbO enters the network with PbO$_4$ structural units by sharing the corners of phosphate network which in turn form P–O–Pb linkages. When PbO acts as network modifier Pb is octahedrally coordinated and behaves like any other conventional alkali oxide modifier [19, 20]. The mixing of Y$_2$O$_3$ to PbO–P$_2$O$_5$ glasses is expected to increase mechanical, thermal, and chemical stability and constitutes as a good candidate for biomedical and photonic applications [21, 22]. On the other hand, there has been an enormous amount of researches on improving the physical properties of phosphate glasses that make them potential materials for electro-optical applications by introducing a number of transition metal oxides like MoO$_3$, Ag$_2$O or PbO to form binary or ternary glass systems. It was revealed that, molybdenum-phosphate glasses belong to a group of glasses which incorporate distorted octahedral structural units [MoO$_6$] or tetrahedral structural units [MoO$_4$] within the glass network [23–28]. Molybdenum oxide combined with P$_2$O$_5$ forms binary glasses over wide and continuous compositional range [23, 29]. The molybdenum ions exist in at least two stable valence states as Mo$^{5+}$ and Mo$^{6+}$ in the glass network depending upon the chemical composition of the host network. The Mo$^{6+}$ ions participate in the network forming, whereas Mo$^{5+}$ ions act as modifiers. Earlier ESR
studies on the glass systems containing molybdenum ions have predicted that Mo\(^{5+}\) ions are present in octahedral coordination along with distorted octahedrons approaching tetragons. Further, Mo-O bond in molybdenum hexavalent oxide is identified as significantly covalent [30, 31]. A considerable number of recent studies on various physical properties viz., spectroscopic, d.c conductivity, dielectric properties, etc., of variety of glass systems containing molybdenum ions are available in the literature [32–37]. Molybdenum oxide is aodour less white or slightly yellow to slightly bluish powder. In the gas phase, three oxygen atoms are double bonded to the central molybdenum atom. In the solid state, anhydrous MoO\(_3\) is composed of layers of distorted MO\(_6\) octahedra in an orthorhombic crystal. The octahedra share edges and form chains which are cross-linked by oxygen atoms to form layers. The octahedra have one short molydenum-oxygen bond to a non-bridging oxygen [38].

![Fig 3.1 MoO\(_3\) structure](image)

The image (Fig. 3.1) shows a section of the chain made up from edge sharing distorted octahedra. The oxygen atoms are above and below the chain link to other chains to build the layer. MoO\(_3\) is used as a component of the co-catalyst used in the industrial production of acrylonitrile by the oxidation of
propene and ammonia. Because of its layered structure and the ease of the Mo(VI)/Mo(V) couple, MoO₃ is of interest in electrochemical devices and displays[39].

MoO₃ based glasses have been the subject of many investigations due to their catalytic properties. The ions of molybdenum inculcate high activity and selectivity in a series of oxidation reactions of practical importance in the glass matrices [40, 41]. A considerable number of interesting studies are available on the environment of molybdenum ion in various inorganic glasses [42–48].

Mo–O bond in molybdenum hexavalent oxide is identified as significantly covalent. The Mo ion exists in at least two stable valence states viz., Mo (V) and Mo (VI) in the glass network. Earlier ESR studies on the glasses containing molybdenum ions have identified the presence of octahedrally coordinated Mo (V) ions along with distorted octahedrons approaching tetragons [49, 50]. These ions act both as network formers as well as network modifiers depending upon their concentration and nature of the host network. The Mo⁶⁺ ions are expected to participate in the glass network with tetrahedral MoO²⁻₄ structural units and may alternate with BO₄ tetrahedral units in MoO₃–B₂O₃ glass matrix. Most of the studies available on MoO₃ containing glasses are on the understanding of their structure by spectroscopic investigations [51–55] and ionic conductivity studies [56]. Few studies on the influence of molybdenum ions on dielectric properties of some glass systems are also available [57–59].
The objective of this paper is to have a comprehensive understanding over the topology and valence states of molybdenum ions in PbO–Y₂O₃–P₂O₅ 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:

- **M₀**: 40PbO–10Y₂O₃–50P₂O₅
- **M₁**: 40PbO–9Y₂O₃–50P₂O₅: 1MoO₃
- **M₂**: 40PbO–8Y₂O₃–50P₂O₅: 2MoO₃
- **M₃**: 40PbO–7Y₂O₃–50P₂O₅: 3MoO₃
- **M₄**: 40PbO–6Y₂O₃–50P₂O₅: 4MoO₃
- **M₅**: 40PbO–5Y₂O₃–50P₂O₅: 5MoO₃

### 3.2. Brief review of previous work on MoO₃ doped glasses

A. Agarwal et al [60] have been prepared alkali molybdo-borate glasses doped with V₂O₅ and studied the influence of MoO₃ on electrical conductivity, electron paramagnetic resonance (EPR) and optical spectra. Y.M. Hamdy et al [61] studied optical and infrared absorption spectra of prepared molybdenum ions in sodium silicophosphate host glasses were investigated before and after gamma irradiation. Reported MoO₃ doped glasses exhibit extra characteristic absorption bands due to the presence of molybdenum ions in three possible valence states, the trivalent, pentavalent and hexavalent forms. A.M. Abdelghany et al [62] prepared Borophosphate
glasses containing different concentrations of molybdenum oxide. Investigated Infrared and UV–visible absorption spectroscopic measurements before and after gamma irradiation. S. Rada et al [63] synthesized and characterized glasses and glass ceramics of the \( x \text{MoO}_3(100−x)[7\text{GeO}_2·3\text{PbO}] \) system where \( x = 0–30 \) mol\% \( \text{MoO}_3 \). Discussed FTIR, UV–vis and EPR data are in view of the glass network structural changes determined by the evolution of molybdenum ions state, glass composition and \( \text{MoO}_3 \) concentration. Sherief M et al [64] studied structure and optical properties of \( \text{MoO}_3 \)-doped lead borate glasses which contain high \( \text{PbO} \) content. N. S. Vedeanu et al [65] studied two glass systems \( x(\text{CuO}·\text{V}_2\text{O}_3) (100−x) [\text{P}_2\text{O}_5·\text{CaO}] \) and \( x(\text{Fe}_2\text{O}_3\text{MoO}_3) (1−x)[2\text{P}_2\text{O}_5\text{PbO}] \) with \( 0.5 \leq x \leq 50 \) mol\% and investigated by EPR method. A. V. Ravi Kumar et al [66] prepared \( \text{Na}_2\text{SO}_4–\text{B}_2\text{O}_3–\text{P}_2\text{O}_5 \) glasses doped with different concentrations of \( \text{MoO}_3 \) and investigated using optical absorption, ESR, and IR spectroscopy. N. Ch. Ramesh Babu et al [67] studied optical absorption and photo luminescence spectra (PL) of the glasses possessing compositions \( (49–x)\text{Li}_2\text{O}–x\text{Y}_2\text{O}_3–50\text{SiO}_2:1.0 \ \text{Ce}_2\text{O}_3/1.0\text{Yb}_2\text{O}_3 \) and \( (49–x)\text{Li}_2\text{O}–x\text{Y}_2\text{O}_3–50\text{SiO}_2:(0.5 \ \text{Ce}_2\text{O}_3 + 0.5 \ \text{Yb}_2\text{O}_3) \) with \( x \) varying from 5 to 15 mol\%. The increase in the rate of energy transfer from \( \text{Ce}^{3+} \) to \( \text{Yb}^{3+} \) could be observed with increasing \( \text{Y}_2\text{O}_3 \) content. Yasser B. Saddeek et al [68] have been synthesized molybdenum lead phosphate glasses doped with \( \text{La}_2\text{O}_3 \) and studied by FTIR, ultrasonic and differential scanning calorimetry (DSC) in order to investigate the role of \( \text{MoO}_3 \) content on their atomic structure. Aleksandrov et al [69] Prepared molybdenum oxide (\( \text{MoO}_3 \))-containing
glasses of $x$MoO$_3$–50ZnO–(50–$x$)B$_2$O$_3$ ($x = 10$, 20, and 30. The main valence of Mo ions in the glasses is found to be Mo$^{6+}$ from X-ray photoelectron spectroscopy measurements. Jiri subcik et al [70] investigated ZnO–B$_2$O$_3$–P$_2$O$_5$ glasses doped with MoO$_3$. Reported the incorporation of MoO$_3$ into the parent zinc borophosphate glass results in a weakening of bond strength in the structural network, which induces a decrease in chemical durability and glass transition temperature. A. Padmanabham et al [71] studied PbO–Sb$_2$O$_3$–As$_2$O$_3$: MoO$_3$ glasses. The X-ray diffraction, the scanning electron microscope, the differential thermal analysis, and the infrared (IR) spectral studies are reported.

M. V. N. Padma Rao et al [72] prepared CaF$_2$–PbO–P$_2$O$_5$ glasses containing different mole fractions of MoO$_3$ and studied Magnetic susceptibility, ESR and Optical absorption, spectral studies on these glasses. L. Srinivasa Rao et al [73] have studied Li$_2$O–MoO$_3$–B$_2$O$_3$ glasses mixed with different concentrations of CuO. The samples were characterized by X-ray diffraction, scanning electron microscopy and differential scanning calorimetry. Optical absorption, luminescence, ESR, IR and dielectric properties. Cozar et al [74] studied local symmetry and interaction between paramagnetic ions in $x$MoO$_3$(1–$x$)[2 P$_2$O$_5$PbO] glasses with 0.5 ≤ $x$ ≤ 50 mol% are investigated by EPR spectroscopy. L. Bih et al [75] have been prepared and characterized two series of glasses, one with varying Li$_2$O:P$_2$O$_5$ ratio and the other with varying Mo:P ratio. P. Syam Prasad et al [76] have been prepared PbO–MoO$_3$–B$_2$O$_3$ glasses containing various proportions of NiO and characterized by differential thermal analysis, spectroscopic and dielectric
properties. Srinivasa Rao et al [77] have been prepared Li$_2$O–MoO$_3$–B$_2$O$_3$ glasses containing different amounts of V$_2$O$_5$, and studied with dielectric properties as a function of the concentration of vanadium ions. Syam Prasad et al [78] have been investigated variety of physical properties including dielectric constant, optical absorption, luminescence, electron spin resonance (ESR) and infrared spectra of a TiO$_2$-doped lead molybdenum borate glass system. Little Flower et al [79] studied structural investigations of PbO–P$_2$O$_5$–Sb$_2$O$_3$ glasses with MoO$_3$ by differential thermal analysis, infrared, optical absorption, Raman and ESR spectra, magnetic susceptibility and dielectric properties. Sreedhar et al [80] prepared lithium fluorophosphate (LFP) glasses doped with 1 mol% MoO$_3$ and characterized by various experimental methods. Syam Prasad et al [81] prepared PbO–B$_2$O$_3$ glasses containing different concentrations of MoO$_3$ and studied dielectric properties. The results of these studies were analyzed with the aid of data on optical absorption, magnetic susceptibilities, ESR and IR spectra of these glasses.

Bih et al [82] have reported the electrical properties of Na$_2$O–MoO$_3$–TeO$_2$ glasses. El-Hofy and Hager et al [83] have studied ionic conductivity in MoO$_3$–BaF–AgI–LiF glasses and concluded that the basic glass constituting units are MoO$_6$ and MoO$_4$ structural groups. Machida et al [84] has investigated local environment of molybdenum ion in AgI–Ag$_2$O–MoO$_3$ glasses by NIR–FT Raman spectroscopy and FT–IR spectroscopy and showed that MoO$_6$ octahedra are linked to MoO$_4$ tetrahedra in these glasses. Boudlich et al [85] have studied MO$^{5+}$ ions as EPR structural probe in phosphate glasses.
and their studies confirmed the distorted octahedral environment of MO$^{5+}$ ions in these glasses.

Qiu et al [86] have studied the electrical properties of molybdenum containing Fe$_2$O$_3$-TeO$_2$ glasses, from these studies they have concluded that the electrical conduction in these glasses was due to small polaron hoping. Khattak et al [87] have reported the structure of molybdenum phosphate glasses by X-ray photoelectron spectroscopy and proposed a structural model basing on the amount of Mo$^{6+}$ reduced to Mo$^{5+}$. Muthupari and Rao et al [88] have performed thermal and infrared spectroscopic studies on Na$_2$O–P$_2$O$_5$ glasses doped with MoO$_3$ and proposed a structural model based on infrared spectroscopy. Jamnicky et al [89] have reported the structure of Cu$_2$O–P$_2$O$_5$ glasses containing MoO$_3$ using infrared spectroscopy and concluded that the structure of these glasses depends strongly on composition of the glass matrix. Sekiya et al [90] have investigated molybdenum containing borate glasses by differential thermal analysis and Raman spectroscopy, they have concluded that the concentration of MoO$_6$ basic structural units depends on the contents of molybdenum ions in these glasses. Ingram et al [91] have investigated structural recovery in AgI–Ag$_2$O glasses containing molybdenum oxide by differential scanning calorimetry. Additionally, a large number of recent interesting studies are available on the influence of molybdenum ions in a variety of other glass systems [92–104].
3.3 Characterization

3.3.1 XRD

Our visual examination of the samples, absence of peaks in the X–Ray diffraction and SEM pictures is clearly suggest that the samples prepared are of amorphous in nature is shown in Figs. 3.2 and 3.3.

![XRD Profile](image)

**Fig. 3.2** XRD Profile of PbO–Y₂O₃–P₂O₅: MoO₃ glasses recorded at room temperature.

![SEM Pictures](image)

**Fig. 3.3** Scanning electron microscopic pictures of PbO–Y₂O₃–P₂O₅ glasses containing different concentrations of MoO₃
3.3.2 Physical Parameters

The physical parameters such as molybdenum ion concentration $N_i$ and mean molybdenum ion separation $r_i$, molar volume ($V_M$) of these glasses are valuated from the measured values of density $d$ and calculated average molecular weight $\overline{M}$, using the conventional formulae and are presented in Table 3.1.

Table 3.1
Physical parameters of PbO–Y$_2$O$_3$–P$_2$O$_5$: MoO$_3$ glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>Density $d$ (g/cm$^3$)</th>
<th>Molar Volume (cm$^3$)</th>
<th>Dopant ion conc. $N_i$ (x10$^{20}$ ions/cm$^3$)</th>
<th>Interionic distance $R_i$ (Å)</th>
<th>Polaron radius $R_p$ (Å)</th>
<th>Field Strength $F_i$ (10$^{15}$, cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M$_0$</td>
<td>5.1829</td>
<td>35.28</td>
<td>1.553</td>
<td>18.61</td>
<td>16.08</td>
<td>0.232</td>
</tr>
<tr>
<td>M$_1$</td>
<td>5.1798</td>
<td>35.14</td>
<td>1.560</td>
<td>18.58</td>
<td>16.05</td>
<td>0.233</td>
</tr>
<tr>
<td>M$_2$</td>
<td>5.1767</td>
<td>35.00</td>
<td>1.567</td>
<td>18.55</td>
<td>16.03</td>
<td>0.234</td>
</tr>
<tr>
<td>M$_3$</td>
<td>5.1736</td>
<td>34.87</td>
<td>1.574</td>
<td>18.52</td>
<td>16.00</td>
<td>0.234</td>
</tr>
<tr>
<td>M$_4$</td>
<td>5.1706</td>
<td>34.73</td>
<td>1.581</td>
<td>18.49</td>
<td>15.98</td>
<td>0.235</td>
</tr>
<tr>
<td>M$_5$</td>
<td>5.1673</td>
<td>34.59</td>
<td>1.553</td>
<td>18.61</td>
<td>16.08</td>
<td>0.232</td>
</tr>
</tbody>
</table>

3.3.3 Differential thermal analysis (DTA) studies

In the Fig. 3.4 DTA scans for PbO–Y$_2$O$_3$–P$_2$O$_5$ glasses doped with different concentrations MoO$_3$ are presented, all the traces exhibited typical glass transition with the inflection point. The DTA traces of these glasses exhibit an endothermic effect due to the glass transition temperature $T_g$.
between 380 and 405°C, followed by an exothermic peak \( T_c \) due to crystal growth. From the measured values of \( T_g \), \( T_c \) the parameter \( (T_c - T_g) \) that gives the information of the stability against devitrification is evaluated and presented in Table 3.2. Among all the glasses, the glass \( M_5 \) (glass containing 5 mol% of MoO\(_3\)), exhibited the lowest value of \( (T_c - T_g) \).

**Table 3.2**

Summary on data of DTA studies of PbO–Y\(_2\)O\(_3\)–P\(_2\)O\(_5\): MoO\(_3\) 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>( M_1 )</td>
<td>405</td>
<td>790</td>
<td>385</td>
</tr>
<tr>
<td>( M_2 )</td>
<td>401</td>
<td>782</td>
<td>381</td>
</tr>
<tr>
<td>( M_3 )</td>
<td>394</td>
<td>773</td>
<td>379</td>
</tr>
<tr>
<td>( M_4 )</td>
<td>387</td>
<td>763</td>
<td>376</td>
</tr>
<tr>
<td>( M_5 )</td>
<td>380</td>
<td>752</td>
<td>372</td>
</tr>
</tbody>
</table>
Fig 3.4 DTA Traces of PbO-Y2O3-P2O5:MoO3 glasses and inset shows the variation of the glass transition temperature $T_g$ and $(T_C-T_g)$ with the concentration of MoO3
3.4 Results

3.4.1 Optical absorption spectra

Fig. 3.5(a) presents optical absorption spectra of PbO–Y₂O₃–P₂O₅:MoO₃ glasses samples recorded at room temperature in the wavelength region 300–1000 nm. The absorption edge observed at 336 nm for glass M₀ (pure glass). It is observed to shift towards slightly higher wavelength side with increase in the concentration of MoO₃. This spectra exhibits a broad absorption band in the region 600-810nm due to the excitation of Mo⁵⁺ (4d¹) ion, with increase in the concentration of MoO₃ the peak height of these bands are observed to increase. The cut off wavelengths, band positions and optical band gaps of the present glass systems are shown in Table 3.3.

From the observed absorption edges, we have evaluated the optical band gaps (Eₒ) of these glasses by drawing Urbach plots (3.5(b)) between \( \alpha (\omega) \hbar \omega = C (\hbar \omega - E₀)² \) as per the equation.

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

(3.1)

From the extrapolation of the linear portion of the curves of Fig.3.5 (b), represents the Urbach plots of all these glasses in which a considerable part of each curve is observed to be linear. The values of optical band gap (Eₒ) obtained from the extrapolation of these curves are presented in Table 3.3, the value of E₀ showed an decreasing trend with the lowest for glass M₅ that shown in inset of Fig.3.5 (b).
Fig. 3.5 (a) Optical absorption spectra of PbO–Y₂O₃–P₂O₅: MoO₃ glasses recorded at room temperature.
Fig 3.5(b) Urbach plots of PbO–Y$_2$O$_3$–P$_2$O$_5$:MoO$_3$ glasses. Inset shows the variation of optical band gap with the concentration of MoO$_3$. 
Table 3.3
Data on optical absorption spectra of PbO–Y₂O₃–P₂O₅: MoO₃ glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Cut-off wavelength (nm)</th>
<th>Optical Band gap $E_o$ (eV)</th>
<th>Band position (nm) of Mo⁵⁺ ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>M₁</td>
<td>367</td>
<td>3.10</td>
<td>724</td>
</tr>
<tr>
<td>M₂</td>
<td>382</td>
<td>3.08</td>
<td>733</td>
</tr>
<tr>
<td>M₃</td>
<td>389</td>
<td>3.02</td>
<td>739</td>
</tr>
<tr>
<td>M₄</td>
<td>397</td>
<td>2.93</td>
<td>744</td>
</tr>
<tr>
<td>M₅</td>
<td>406</td>
<td>2.86</td>
<td>746</td>
</tr>
</tbody>
</table>

3.4.2 ESR spectra

ESR spectra of PbO–Y₂O₃–P₂O₅ glasses doped with different concentration of MoO₃ recorded at room temperature are shown in Fig. 3.6. The spectra exhibit a central line surrounded by smaller satellites with $g_\perp = 1.934$ and $g_\parallel = 1.888$ due to paramagnetic Mo⁵⁺ ion. They may be attributed to the $^{95}\text{Mo} (15.7\%)$ and $^{97}\text{Mo} (9.4\%)$ isotopes which have the nuclear spin $I = 5/2$. The intense central line belongs to the $^{96}\text{Mo}$ isotope which has the nuclear spin $I = 0$. The intensity and the half width $\Delta B_{1/2}$ of the central line is found to increase with increase in the concentration of MoO₃ (Fig. 3.6). Further the resolution of the hyperfine splitting goes on decreasing with increase in the concentration of MoO₃. The values ESR parameters for some other disordered compounds (Table 3.4), the parameters obtained for the glasses are similar.
Table 3.4
Data on ESR spectra PbO–Y₂O₃–P₂O₅: MoO₃ glasses

| Glass | g_{||} | g_{⊥} |
|-------|-------|-------|
| M₁    | 1.878 | 1.924 |
| M₂    | 1.880 | 1.926 |
| M₃    | 1.882 | 1.929 |
| M₄    | 1.885 | 1.930 |
| M₅    | 1.888 | 1.934 |
Fig. 3.6. ESR Spectra of PbO–Y$_2$O$_3$–P$_2$O$_5$:MoO$_3$ glasses recorded at room temperature.
3.4.3 IR spectra

The Infrared spectra of the PbO–Y2O3–P2O5 glasses doped with different concentrations of MoO3 (Fig. 3.7). The infrared spectra of the studied glasses showed some different frequency regions. The bands located at around 1289–1311 cm\(^{-1}\) are assigned to the bending vibrations of PO\(^2\) groups [105]. These bands may be overlapped with a band assigned to the vibration of PbO\(_6\) structural units. The last units have a modifier role. The bands at around 867–888 cm\(^{-1}\) are assigned to symmetric stretching vibrations of P–O–P rings [106]. Two bands have also located at 885 and 825 cm\(^{-1}\) in the spectrum, these bands are identified due to \(\gamma_1\) (symmetric stretching vibrations) and \(\gamma_2\) (doubly degenerate stretching vibrations) vibrational modes of MoO\(_4\) groups [107] that take part in the glass network forming positions. The bands at around 1113–1136 cm\(^{-1}\) are related to P–O–P asymmetric stretching vibrations of bridging oxygen atoms in P–O–P bands. The band at around 1035 cm\(^{-1}\) which is attributed to vibrations of PO\(_4^{3-}\) groups. The vibrational bands around 1256 cm\(^{-1}\) are attributed to symmetric stretching mode of P = O [108]. The summary of data on IR spectra is presented in Table 3.5.
Table 3.5
Summary of data on band positions in IR spectra of PbO–Y$_2$O$_3$–P$_2$O$_5$: MoO$_3$ glasses.

<table>
<thead>
<tr>
<th>Glass sample</th>
<th>PO$^{2-}$ asym.</th>
<th>P–O–P Asym. stretching</th>
<th>PO$_4^{3-}$ groups</th>
<th>P–O–P sym. stretch. &amp; MoO$_4$ units</th>
<th>MoO$_6$ units</th>
<th>Pb–O units</th>
</tr>
</thead>
<tbody>
<tr>
<td>M$_1$</td>
<td>1311</td>
<td>1113</td>
<td>934</td>
<td>867</td>
<td>796</td>
<td>462</td>
</tr>
<tr>
<td>M$_2$</td>
<td>1305</td>
<td>1122</td>
<td>940</td>
<td>875</td>
<td>805</td>
<td>458</td>
</tr>
<tr>
<td>M$_3$</td>
<td>1299</td>
<td>1127</td>
<td>943</td>
<td>878</td>
<td>812</td>
<td>455</td>
</tr>
<tr>
<td>M$_4$</td>
<td>1291</td>
<td>1133</td>
<td>948</td>
<td>884</td>
<td>816</td>
<td>449</td>
</tr>
<tr>
<td>M$_5$</td>
<td>1287</td>
<td>1136</td>
<td>951</td>
<td>888</td>
<td>823</td>
<td>444</td>
</tr>
</tbody>
</table>
Fig. 3.7 IR spectra of PbO-Y$_2$O$_3$-P$_2$O$_5$: MoO$_3$ glasses recorded at room temperature.
3.5 Discussion

$\text{P}_2\text{O}_5$ is a well-known strong glass forming oxide, participates in the glass network with $\text{PO}_4$ structural units. One of the four oxygen atoms in $\text{PO}_4$ tetrahedron is doubly bonded to the phosphorous atom with the substantial $\pi$-bond character to account for pentavalency of phosphorous. The $\text{PO}_4$ tetrahedrons are linked together with covalent bonding in chains or rings by bridging oxygen’s. Neighboring phosphate chains are linked together by cross bonding between the metal cation and two non-bridging oxygen atoms of each $\text{PO}_4$ tetrahedron; in general, the $\text{P}–\text{O}–\text{P}$ bond between $\text{PO}_4$ tetrahedra is much stronger than the cross bond between chains via the metal cations [109].

$\text{PbO}$ in general is a glass modifier and enters the glass network by breaking up the $\text{P}–\text{O}–\text{P}$ (normally the oxygen’s of $\text{PbO}$ break the local symmetry while $\text{Pb}^{2+}$ ions occupy interstitial positions) and introduces coordinate defects known as dangling bonds along with non bridging ions. In this case the lead ions are octahedrally positioned. To form octahedral units, $\text{Pb}$ should be $sp^3d^2$ hybridized ($6s$, $6p$ and $6d$ orbital’s) [110, 111]. However $\text{PbO}$ may also participate in the glass network with $\text{PbO}_4$ structural units when lead ion is linked to four oxygen’s in a covalent bond configuration. In such a case the network structure is considered to build up from $\text{PbO}_4$ and $\text{PO}_4$ pyramidal units, with $\text{P}–\text{O}–\text{Pb}$ linkages shown in IR spectra.

Molybdenum ions are expected to exist mainly in the $\text{Mo}^{5+}$ state in the present $\text{PbO–Y}_2\text{O}_3–\text{P}_2\text{O}_5$ glass network. However, the increment of $\text{Mo}^{5+}$ state is viable during melting and subsequent annealing process. Our visual examination showed that as the mole fraction of $\text{MoO}_3$ is increased; the color
of the glass became increasingly blue, indicating a progressive increment of molybdenum ions from the Mo$^{6+}$ state to the Mo$^{5+}$ state. These Mo$^{5+}$ ions are quite stable and occupy octahedral positions with distortions due to the Jhon-Teller effect [112, 113]. With increase in the concentration of MoO$_3$, the value of the glass transition temperature $T_g$ and parameter $(T_c-T_g)$ that gives the information on the glass forming ability, have been observed to decrease gradually. Normally, the decrease in bond length, cross-link density and closeness of packing, are responsible for such a decrease of these parameters. The manifestation of these results is that, with the increasing concentration of MoO$_3$ in the glass network, there is increasing concentration of molybdenum ions that exist in Mo$^{5+}$ state, occupy modifying positions, reduce to cross-link density and weaken the bond strength.

The IR analysis of binary PbO–P$_2$O$_5$ glasses the existence of PO$_4$ joined by one P–O–P bonds. Addition of PbO depolymerize a number of phosphorous-oxygen’s chains by forming new P–O–Pb bonds and non bridging oxygen’s in the glass network, and Pb$^{2+}$ ions will occupy positions between P–O–P layers by forming ionic bonding. The intensity of bands due to PO$_2^-$ groups and PO$_4^{3-}$ groups are observed to grow at the expense of symmetric stretching P=O bonds and P–O–P rings. The band due to $\nu_1$ vibrational mode of MoO$_4^{2-}$ tetrahedral units located at about 890 cm$^{-1}$ is observed to be shifted towards a region of higher wave number, in this region the band due to partially isolated Mo–O bonds of the strongly deformed MoO$_6$ groups is expected [114]. Similarly the $\nu_3$ vibrational band of MoO$_4^{2-}$ units observed at
about 836 cm\(^{-1}\) in the spectra is shifted towards on the region of asymmetric stretching vibrations of Mo–short O\(_{\text{long}}\)–Mo bridge associated with MoO\(_6\) octahedra containing Mo=O bond [114]. These results confirm a gradual transformation of molybdenum ions from tetrahedral positions to octahedral positions with increase in the concentration of MoO\(_3\). Broad absorption band observed in the region of 600–900 nm in the optical absorption spectra of these glasses is attributed to the excitation of Mo\(^{5+}\) (4d\(^1\)) ion. In fact for this ion two optical excitations were predicted starting from b\(_2\) (d\(_{xy}\)) ground state to (d\(_{x^2−y^2}\)) and (d\(_{x^2−y^2}\)) with E\(_1\) = 15,000cm\(^{-1}\) and E\(_2\) = 23,000cm\(^{-1}\) [115]. Perhaps, due to inter charge transfer (Mo\(^{5+}\)↔Mo\(^{6+}\)) in the glass network, the resolution of these transitions could not be observed. The highest intensity of this band observed in the spectrum of glass M\(_5\) points out that the presence of the highest concentration of Mo\(^{5+}\) ions in this glass M\(_5\). Such Mo\(^{5+}\) ions may form Mo\(^{5+}\)O\(_3\)- molecular orbital states and are expected to participate in the depolymerisation of the glass network [116–118] creating more bonding defects and non-bridging oxygen’s (NBO’s). Normally, the oxygen’s of Mo\(^{5+}\)O\(_3\)- complexes break the local symmetry while molybdenum ions go in the interstitial positions. Hence the gradual increase in the concentration of molybdenum ions in the glass network localized electrons originally trapped on Mo\(^{5+}\) sites begin to overlap with the empty 3d states on the neighboring Mo\(^{6+}\) sites. Causes a creation of large number of donor centers; subsequently, the excited states of as a result, the impurity band becomes more extended into the main band gap. This development shifts the absorption edge to low energy side, resulting a
significant shrinkage in the band gap. This may explain the decrease in the optical band gap with increase in the mole fraction of MoO$_3$.

The highest intensity of the signal observed in the ESR spectrum of the glass M$_5$ suggests the presence of the highest concentration of Mo$^{5+}$O$_3^-$ complexes. The values of $g_\perp$ and $g_\parallel$ from this spectrum have been found to be dependent on the concentration of the MoO$_3$, the structural disorder arising from the site-to-site fluctuations of the local surroundings of the paramagnetic Mo$^{5+}$ ions can be accounted for such variations. The variation of MoO$_3$ content has considerably affected the intensity of the signal; in fact, the signal is observed to be feeble for the samples with lower concentration of MoO$_3$.

### 3.6 Conclusions

PbO–Y$_2$O$_3$–P$_2$O$_5$ glasses mixed with different concentrations of MoO$_3$ (ranging from 0 to 5.0 mol%) were synthesized. A variety of properties viz., Physical, DTA and spectroscopic properties that include optical absorption, ESR, IR have also been investigated.

1. The differential thermal analysis of these samples has indicated decrease glass forming ability with increase in the concentration of MoO$_3$.

2. The IR spectra studies of these samples have exhibited bands due to MoO$_3$ and MoO$_6$ structural units in addition to the conventional bands due to various symmetrical and asymmetrical phosphate, PO$_4$ and PO$_6$ structural groups. With increasing the concentration of MoO$_3$, the intensity of symmetrical bands is observed to grow at the expense of asymmetric bands; from these results it is concluded that there is a increasing degree of disorder in the glass network.
3. The Optical absorption studies the impurity band becomes more extended into the main band gap. This development shifts the absorption edge to low energy side, resulting a significant shrinkage in the band gap. This may explain the decrease in the optical band gap with increase in the mole fraction of MoO$_3$.

4. The ESR studies indicated that the variation of MoO$_3$ content has considerably affected the intensity of the signal; in fact, the signal is observed to be feeble for the samples with lower concentration of MoO$_3$. 
References


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