Summary and Conclusions

This chapter contains a brief outlines and conclusions drawn from the investigations carried out on spectroscopic, non-linear optical properties of PbO–Y2O3/Sc2O3/La2O–P2O5 glasses containing certain transition metal (viz., molybdenum, tungsten and chromium) ion system is also included.
Summary and Conclusions

6.1 Summary

A systematic study on infrared, optical absorption and ESR spectra and magnetic properties of certain transition metal ions doped with PbO–M₂O₃–P₂O₅ (where M₂O₃ = Y₂O₃, La₂O₃ and Sc₂O₃) glasses has been presented.

The glasses used for the present study are:

Series 1: 40 PbO – (10–x) Y₂O₃–50P₂O₅: x MoO₃ (0 ≤ x ≤ 5.0 wt %)

Series 2: 40 PbO – (10–x) La₂O₃–50P₂O₅: x Cr₂O₃ (0 ≤ x ≤ 0.5 wt %)

Series 3: 40 PbO – (10–x) Sc₂O₃–50P₂O₅: x WO₃ (0 ≤ x ≤ 5.0 wt %)

The glasses were prepared by the usual melting, quenching and subsequent annealing techniques.

The following studies were made:

(a) Infrared spectra

(b) Optical absorption

(c) ESR spectra

(e) Magnetic susceptibility and magnetic moments

The samples were characterized by X-Ray diffraction and differential thermal analysis techniques.

The following measurements were taken:

1) Optical absorption spectra of the samples were recorded at room temperature in the wavelength range 300-1000 nm

2) Electron spin resonance spectra of glasses doped with transition metal
ions at room temperature.

3) Infrared spectra of all these glasses in the region 400 to 2000 cm\(^{-1}\).

4) Magnetic susceptibility at room temperature and subsequent evaluation of magnetic moments for series 2 glasses.

6.2 Conclusions

The main conclusions drawn from the results of above studies are summarized below:

1. The **differential thermal analysis** results suggests that the glass forming ability is decreases with increasing concentrations of MoO\(_3\) in case of series 1 glasses. In series 2 glasses increasing glass forming ability when the concentration of Cr\(_2\)O\(_3\) is greater than 0.3mol% and in series 3 glasses the glass forming ability is high for the glass containing 5mol% of WO\(_3\).

2. In **Infrared Spectrum** of series 1, the bands located at around 1289–1311 cm\(^{-1}\) is assigned to the bending vibration of PO\(^{-2}\) groups. The bands at around 867–888 cm\(^{-1}\) are assigned to symmetric stretching vibrations of P–O–P rings. 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 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. 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. 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$_{\text{short}}$–O$_{\text{long}}$–Mo bridge associated with MoO$_6$ octahedra containing Mo=O bond. These results confirm a gradual transformation of molybdenum ions from tetrahedral positions to octahedral positions with increase in the concentration of MoO$_3$.

The infrared spectra of series 2 glasses exhibit vibrational bands at about 1250 cm$^{-1}$ (identified due to P–O stretching vibration, this region may also consist of bands due to antisymmetrical vibrations of PO$_2^-$ groups), 1050 cm$^{-1}$ (a normal vibrational mode in PO$_4^{3-}$ group arising out of $\gamma_3$-symmetric stretching), at 720 cm$^{-1}$ (due to P–O–P symmetric bending vibrations) and another band at 545 cm$^{-1}$ due to O=P–O vibrations. A band due to PbO$_4$ structural units with the growing intensity with the concentration of Cr$_2$O$_3$ (especially beyond 0.3mol%) is also observed in the spectra of all these glasses at about 470 cm$^{-1}$. With the introduction of Cr$_2$O$_3$ (up to 0.3mol%), the intensity of bands due to P=O, PO$_4^{3-}$ and P–O–P is observed to decrease, for further increase of Cr$_2$O$_3$ content, the intensity of these bands is observed
to increase. Additionally, in the spectra of glasses especially C\textsubscript{3} to C\textsubscript{5}, a band at about 890 cm\textsuperscript{-1} due to $\gamma_3$ vibrations of CrO\textsubscript{4}\textsuperscript{2−} structural units (the intensity of which is increasing with the concentration of Cr\textsubscript{2}O\textsubscript{3}) is also observed. With the increase in the concentration of Cr\textsubscript{2}O\textsubscript{3} up to 0.3 mol% the intensity of the bands due to P=O, PO\textsubscript{4}\textsuperscript{3−} and P–O–P symmetric bending vibrations is observed to decrease. Whereas the intensity of the band due to PO\textsubscript{4} bending torsional vibrational band is observed to increase. These results suggest that in this concentration range chromium ions mostly exist in trivalent state, and act as modifiers and disturb the glass network. However, when the concentration Cr\textsubscript{2}O\textsubscript{3} is raised beyond 0.3 mol%, the chromium ions seem to exist in Cr\textsuperscript{6+} state (evidenced from optical absorption spectra), and participate in the glass network forming with CrO\textsubscript{4}\textsuperscript{2−} structural units, alternate with PO\textsubscript{4} units, such linkages may be responsible for the observed increase in the intensity of the symmetrical bands mentioned above in IR spectra series 2 glasses.

In infrared spectra series 3 glasses, the bands located at around 1301–1324 cm\textsuperscript{-1} are assigned to the bending vibrations of PO\textsuperscript{2−} groups. These bands may be overlapped with a band assigned to the vibration of PbO\textsubscript{6} structural units. The last units have a modifier role. The bands at around 790-803 cm\textsuperscript{-1} are assigned to symmetric stretching vibrations of P–O–P rings. The spectra of the glasses containing WO\textsubscript{3}, have exhibited three additional bands due to $\nu_1$-WO\textsubscript{4}, $\nu_4$-WO\textsubscript{4} and $\nu_1$-WO\textsubscript{6} vibrations at about 942 cm\textsuperscript{-1}, 432 cm\textsuperscript{-1} and 987 cm\textsuperscript{-1} respectively. The bands at around 878 cm\textsuperscript{-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. 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 $\nu_1$-WO$_4$, $\nu_4$-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. The 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.

3. In the absorption spectra of series 1 glasses. The absorption edge observed to shift towards slightly higher wavelength side with increase in the
concentration of MoO$_3$. This spectra exhibits a broad absorption band in the region 600–810 nm due to the excitation of Mo$^{5+}$ (4d$^1$) ion: with increase in the concentration of MoO$_3$ the peak height of these bands are observed to increase. These results confirm a gradual transformation of molybdenum ions from tetrahedral positions to octahedral positions with increase in the concentration of MoO$_3$.

In the case of series 2 glasses, the cutoff wavelength shifted towards higher wavelength with increase in the concentration of Cr$_2$O$_3$ up to 0.3 mol% and there after the edge is shifted gradually towards lower wavelength. The spectrum of glass C$_1$, has exhibited two prominent absorption bands with the peaks at 433nm (peak 1) and 662nm (peak 2), with increasing concentration of Cr$_2$O$_3$ up to 0.3 mol%, no considerable changes in the positions of these bands have been observed. However, beyond this concentration (0.3 mol %), the peak positions of these two bands observed to shift towards slightly lower wavelength with decreasing intensity. Further, an additional kink (the intensity of which is found to increase gradually at the expense of other two prominent peaks) at about 370nm has also been observed in the spectra of glasses C$_4$ and C$_5$. Two additional shoulders at 670 and 700 nm have also been observed on peak-2 of all the glasses. These results indicate a gradual increase in the covalent environment for chromium ions when the concentration of Cr$_2$O$_3$ is raised from 0.3 to 0.5 mol%. Additionally, a pair of weak narrow structures at 670 and 700 nm due to $^4$A$_2$ →$^2$T$_1$ and $^4$A$_2$→$^2$E (spin and parity forbidden)
transitions, respectively, have also been located on \( ^4T_2 \) band in the spectra of these glasses. These bands appear due to spin orbit interaction and mixing between \( ^2E \) and \( ^4T \) and \( ^2T_1 \) and \( ^4T_2 \) levels. Further, a decrease in the widths of \( ^2E \) and \( ^2T_1 \) bands has clearly been observed with increase in the concentration of chromium ions from 0.3 to 0.5 mol\%. Such a decrease indicates a lowering degree of disorder in the glass network, may be due to the decreasing concentration of induced heterogeneous nucleation centers in the glass network that separate and enhance the long range order of chromium and phosphate groups.

For series 3 glasses, the broad band observed in the optical absorption spectra of Lead Scandium Phosphate glasses doped with tungsten ions are recognized due to \( d_{xy} \rightarrow d_{x^2-y^2} \) 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.

4. The ESR spectra, recorded at room temperature for series 1 glasses exhibit a central line surrounded by smaller satellites with $g_{\perp} = 1.934$ and $g_{\parallel} = 1.888$ due to paramagnetic Mo$^{5+}$ ion. They may be attributed to the $^{95}$Mo (15.7%) and $^{97}$Mo (9.4%) isotopes which have the nuclear spin $I = 5/2$. The intense central line belongs to the $^{96}$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 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.

In the case of series 2 glasses, the spectrum of each glass exhibits an intense absorption line centered at $g \sim 1.98$ and a combination of two absorption lines corresponding to $g = 4.29$ and 5.32; with increase in the concentration of Cr$_2$O$_3$ up to 0.3 mol%, an increase in the intensity of low field peak ($g \sim 1.98$) could clearly be observed. The intensity and line width of both the signals are observed to decrease with the increase of Cr$_2$O$_3$ concentration from 0.3 to 0.5 mol%. We have observed the decrease in the intensity of the signal $g.2$, with increase in the concentration of Cr$_2$O$_3$ beyond 0.3 mol%. Such a decrease may be attributed to the following reasons: (i) presence of Cr$_2$O$_3$ microcrystalline which exhibit antiferromagnetic interactions at room temperature [29] and (ii) due to the presence of large concentration of chromium ions in Cr$^{6+}$ state.
ESR spectra of PbO–Sc$_2$O$_3$–P$_2$O$_5$ glasses doped with different concentrations of WO$_3$ recorded at room temperature. exhibited an asymmetric signal (identified due to distorted octahedral W$^{5+}$ ions) at $g_\perp$=1.73 and $g_\parallel$=1.62; As the concentration of WO$_3$ is increased, a slight decay in the intensity of this signal with increase in the concentration of WO$_3$ is visualized; this is attributed to decrease in the concentration of W$^{5+}$ paramagnetic spices with the increase in the concentration of WO$_3$ in the glass networke.

Summing up the entire work presented in this dissertation, it is felt that the study on various optical properties of transition metal oxide doped PbO–M$_2$O$_3$–P$_2$O$_5$ glasses has yielded some valuable information which may be helpful for using these glasses for practical applications.