This chapter presents the general introduction, scope, contents and aim of the present work. In this chapter, the basic theory related to spectroscopic, non-linear optical properties of PbO–Y\textsubscript{2}O\textsubscript{3} /Sc\textsubscript{2}O\textsubscript{3} /La\textsubscript{2}O–P\textsubscript{2}O\textsubscript{5} glasses containing certain transition metal (viz., molybdenum, tungsten and chromium) ion system is also included.
General introduction Scope and Contents of present work

1.1 Introduction

Glass is an inorganic solid material that is usually clear or translucent with different colors it is hard, brittle and stands up to the effects of wind, rain or sun. In more precise terminology, Glass is an amorphous solid completely lacking in long range, periodic atomic structure and exhibiting a region of glass transformation behavior is a glass.

A study of the physical properties of the glasses is of considerable importance because of the insight it gives into the fundamental process-taking place in them. Such a study paved the way for the application of some of these glasses in technology. In fact, the physical properties of the glasses are to a large extent controlled by the structure, composition, and the nature of the bonds of the glasses. The investigation of the changes in the physical properties of glasses with controlled variation of chemical composition, doping etc., is of considerable interest in the application point of view.

Materials prepared from a melt quenching are often referred to as glasses. Unlike crystals, these materials do not possess the long-range periodicity of the arrangement of the atoms. However the building block, \((\text{AO}_3)^{-3}\) triangle, where A stands for metal) or tetrahedra which is known as short-range order, is retained in the glass. These materials possess ionic as well as covalent bonding interaction.

When a liquid is cooled from high temperature, crystallization may take place at the melting point \(T_m\). If the crystallization takes place, there will be
abrupt change in the volume at $T_m$ and if the glass formation takes place, there will be a gradual break in slope. The region over which the change of slope occurs is known as glass transition temperature $T_g$. This process of changes in volume with temperature as a super cooled liquid is cooled through the glass transition temperature $T_g$ is illustrated Fig. 1.1.

**Fig. 1.1** Schematic illustration of the change in volume with temperature as super cooled liquid is cooled through the glass transition temperature $T_g$.

Why do certain materials readily form glasses on cooling a melt and why do only certain chemical compositions of materials have a greater glass-forming tendency? To the present day, the perfect knowledge on the answers of these questions is lacking. However, there are several factors which play a significant role in determining the ease of glass formation, for example,
chemical or structural properties of the glass system, thermodynamic or free volume aspects of the materials, the average atomic coordination number etc.

The credit of first successful attempt to categorize the materials into glass formers and non-glass formers goes to Zachariasen [1]. He prepared the glasses with five oxide materials which are the only known glass formers by themselves: SiO$_2$, GeO$_2$, B$_2$O$_3$, As$_2$O$_3$ and P$_2$O$_5$. In addition, these oxides can also form glasses when mixed up with other oxides (up to certain percentage), which were not by themselves glass formers. Basing on these glasses, Zachariasen proposed certain rules that an oxide should obey if it has to form a glass. The latest rules after Cooper [2] objections to original rules are.

i) A high proportion of glass network forming cations is surrounded by oxygen tetrahedra or triangles.

ii) The oxygen polyhedra share only corners with each other.

iii) Some oxygen atoms are linked to only two cations, and do not form additional bonds with any other cations.

Basing on these rules, a continuous random network for a glass can be constructed as shown in Fig. 1.2. As per these rules, the oxides of the type AO, A$_2$O should not form glasses, and the rules are satisfied only for oxides of the type A$_2$O$_3$, AO$_2$ and A$_2$O$_5$. Oxides such as A$^+$ (example Li$^+$, Na$^+$, K$^+$ etc.,) A$^{2+}$ (example Ca$^{2+}$, Pb$^{2+}$, Cd$^{2+}$ etc.,) other than A$^{3+}$ and A$^{4+}$ are known as network modifiers. Li$_2$O, Na$_2$O, K$_2$O, PbO, CaO, CdO etc., are some of the basic examples of modifiers in glass network. These modifiers break-up the continuous network by introducing non-bridging oxygens (Fig. 1.3). A third
group of oxides known as intermediate class of oxides also exist which by themselves not readily form glasses but do so when mixed with other oxides; such oxides are known as intermediate glass formers. The examples of this group are TeO$_2$, WO$_3$, MoO$_3$, Al$_2$O$_3$, Ga$_2$O$_3$, In$_2$O$_3$, V$_2$O$_5$, etc. Excellent reviews and articles on the topology of the glass by Vogel [3] Elliott [4], Polk [5], Rao [6] Ingram [7], and Shelby [8] give useful information.

**Fig. 1.2** Two dimensional schematic of crystalline and non-crystalline (glass) materials.

**Fig. 1.3** Structure of a glass with modifier oxide
During the last few decades a large variety of inorganic glasses have been developed with an attempt to achieve suitable electrical, mechanical and optical characteristics. These characteristics are associated with the improved physical properties such as electrical resistance, mechanical strength, glass transparency, IR transmission performance and their ability to accept more transition metal ions for their use in solid-state ionic devices. Work along these lines was carried out on a number of glasses giving valuable information [9-16].

Investigations on the spectroscopic properties such as optical absorption, infrared spectra and electron spin resonance can be used as probes to throw some light on the structural aspects of these glasses.

Based on the studies carried out the thesis has been divided into three parts. Part-I deals with spectroscopic and EPR studies on PbO–Y_2O_3–P_2O_5 glasses doped with molybdenum ion, Part-II is devoted to “Magnetic and spectroscopic properties of PbO–La_2O_3–P_2O_5:Cr_2O_3 glass system”, and Part-III deals with “Spectroscopic Investigation of Tungsten Ions in Lead Scandium Phosphate Glass System”.

1.2 Scope of the present work

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 PO_4 structural units with covalent bonding in chains or rings by bridging oxygens [17–20]. 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 [21, 22], have low melting and glass transition temperatures [23, 24], high electrical conductivity [25], high thermal expansion coefficient [26], and high ultraviolet (UV) transmission [27, 28]. These properties making them useful candidates for fast ion conducting materials [29], laser host matrices after doping with rare-earth elements [30, 31], glass-to-metal seals [32], and for the immobilization and disposal of nuclear waste were reported [33, 34]. Investigations of lead phosphate glasses have revealed that the modifier/former role of PbO depends on PbO concentration in the glass composition x PbO (100–x) P2O5 with 0 ≤ x ≤ 85 mol%. The created P–O–Pb bonds along with the high ionic field strength μ and polarizability of Pb2+ ions control the physical properties of lead phosphate glasses. Depending on the studied glass system, the Pb2+ ions show an intermediate character between former and modifier. As a glass former, PbO enters the network with PbO4 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 [35, 36]. 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 MoO3, Ag2O, 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 [MoO6] ortetrahedral structural units
[MoO₄] within the glass network [37–42]. A lot of the current knowledge concerning the structure of matter is based on spectroscopic investigations that offer notable contributions to the atomic and molecular physics, chemistry and molecular biology. Information about the molecular structure and the molecular interactions can be derived from the emission spectra and/or absorption generated when the radiation interacts with the atoms and/or matter molecules. Wavelength measures allow atomic and molecular energy levels determination. The line intensity is proportional to the transition probability that measures how strongly two levels of a molecular (or atomic) transition are coupled. As the transition probability depends on the wave functions of both energy levels, intensity measures are useful to verify the excited electrons space distribution, which can be esteemed from approximate solutions of the Schrödinger equation. The natural width of a line can be solved for special techniques, allowing us to determine average life times of excited molecular states.

The generally poor chemical durability of phosphate glasses has previously hampered large scale investigations of their potential for industrial applications. However, the addition of appropriate modifying cations into the parent P₂O₅ network former is known to produce phosphate glasses with drastically different physical and chemical properties [43–48]. The structure of vitreous P₂O₅ consists of a 3D network of corner-sharing PO₄ tetrahedra, each of which has a P–O (non-bridging O) double bond. The structural instability arises from the energetic imbalance between the dp-pp bonding character in the terminal P–O and the bridging P–O–P configurations which tend to break up
the cross-linking network [49]. The lead-phosphate glass system is one of the more extensively studied cases. Although binary PbO–P₂O₅ glasses near the meta phosphate composition are somewhat susceptible to aqueous corrosion and crystallization at low temperatures [50], their chemical durability can be enhanced dramatically by adding a third metal-oxide component. Moreover, the resulting ternary glasses may exhibit unique properties that are desirable for novel applications. Sales and Boatner [51].

The first row transition metal ions are very interesting ions to probe in the glass network because their outer d-electron orbital functions have rather broad radial distributions and their responses to surrounding actions are very sensitive; as a result these ions influence the physical properties of the glasses to a substantial extent.

Three series of elements are formed by filling the 3d, 4d and 5d shells of electrons. Together these comprise the d-block elements. They are often called ‘transition elements’ because their position in the periodic table is between s-block and p-block elements. Their properties are transitional between the highly reactive metallic elements of the s-block, which typically form ionic compounds, and the elements of p-block, which are largely covalent. In s-and p-blocks, electrons are added to the outer shell of the atom where as in d-block they are added to the penultimate shell. Typically transition elements have an incompletely filled d level.

In the d-block elements, the penultimate shell of electrons is expanding. Thus they have many physical and chemical properties in common and hence
all the transition elements are metals. They are therefore good conductors of electricity and heat have a metallic luster and are hard, strong and ductile. They also form alloys with other metals. One of the most striking features of the transition metal elements is that they usually exist in several different oxidation states (Table 1.1). Furthermore, the oxidation states change in units of one, e.g. Fe$^{3+}$ and Fe$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$.

**Table 1.1**

**Oxidation states of transition metal elements**

<table>
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<tr>
<th>Electronic Structure</th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
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<td>$d^2s^2$</td>
<td>$d^3s^2$</td>
<td>$d^4s$</td>
<td>$d^5s^2$</td>
<td>$d^6s^2$</td>
<td>$d^7s^2$</td>
<td>$d^8s^2$</td>
<td>$d^9s^2$</td>
<td>$d^{10}s^2$</td>
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<td>Oxidation States</td>
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<td>VII</td>
<td>VII</td>
</tr>
</tbody>
</table>

Among the first five transition metal elements, the correlation between the electronic structures and minimum and maximum oxidation states in simple compounds is complete. In the highest oxidation states of these first five elements, all of the s and d electrons are being used for bonding. Thus the properties depend only on size and valency, and consequently show some similarities with elements of the main groups in similar oxidation states. If the $d^5$ configuration is exceeded, i.e. in the last five elements, the tendency for all
the d electrons to participate in the bonding decreases. Thus Fe has a maximum oxidation state of (+VI).

The covalent radii of the elements decrease from left to right across a row in the transition series, until near the end when the size increases slightly. On passing from left to right, extra protons are placed in the nucleus and extra orbital electrons are added. The orbital electrons shield the nuclear charge incompletely (d electrons shield less efficiently than p electrons, which in turn shield less effectively than s electrons). Because of this poor screening by d electrons, the nuclear charge attracts all of the electrons more strongly: hence a contraction in size occurs.

Recently, much attention has been paid to research in inorganic glasses doped with transition metal ions because of their technological importance in the development of tunable solid state lasers, new luminescence materials, solar energy converters and fiber optic communication devices. In view of these, it is felt worthwhile to have some understanding over the spectroscopic properties of PbO–Y₂O₃–P₂O₅, PbO–Sc₂O₃–P₂O₅, PbO–La₂O₃–P₂O₅, glasses containing certain transition metal (viz., molybdenum, tungsten and chromium) ions.

The studies on dielectric properties and the dependence of these properties on the composition, structure and on various external factors such as humidity, radiation effect, mechanical action etc., pave the way for estimating the insulating character. Whereas the investigations on spectroscopic (viz., optical absorption, electron spin resonance and infrared spectra) properties give the information on environment and the oxidation states of the transition metal
ions in the glass network and also help to assess the suitability of these glasses for practical applications.

A preliminary description of the above-mentioned properties along with their relation to some of the investigations (similar to those of present work) on PbO–Y₂O₃–P₂O₅, PbO–Sc₂O₃–P₂O₅, PbO–La₂O₃–P₂O₅ glasses is given below:

1.2.1 Physical parameters

Some physical parameters useful for characterization PbO–Y₂O₃–P₂O₅, PbO–Sc₂O₃–P₂O₅, PbO–La₂O₃–P₂O₅, glasses containing certain transition metal (viz., molybdenum, tungsten and chromium) ions are estimated from the measured value of density (d) and the average molecular weight \( M \), using the following equations [52]:

The transition metal ion concentration \( N_i \) could be obtained from:

\[
(i) \quad N_i \ (10^{22} \text{ ions/cm}^3) = \frac{N_A \ M \ (\text{mol} \%) \ d}{M} \quad (1.1)
\]

From the \( N_i \) values obtained, the polaron radius \( r_p \) and inter–ionic distance \( r_i \) of transition metal ions could be evaluated:

\[
(ii) \quad \text{Inter–ionic distance } r_i (\text{Å}) = \left[ \frac{1}{N_i} \right]^{1/3} \quad (1.2)
\]

\[
(iii) \quad \text{Polaron radius } r_p (\text{Å}) = \left[ \frac{\pi}{2 \times 6N_i} \right]^{1/3} \quad (1.3)
\]
The field strength \(F_i\) of transition metal ion in the glass matrix is described through the oxidation number \(z\) and the ionic radii \(r_p\) of the transition metal ions by:

\[
(iv) \quad \text{Field strength } F_i (\text{cm}^{-2}) = \frac{z}{r_p^2} \quad (1.4)
\]

### 1.2.2 Optical absorption

Optical radiation interacts with materials in a variety of ways depending upon the material and the wavelength of the optical radiation—giving rise to the optical spectra, which could be either emission or absorption spectra in solids, normally it is the absorption spectra, which is observed. This is nothing but the variation of the radiation intensity as a function of wavelength. Study of the absorption spectra of transition metal ions embedded in solids had been extensively used to obtain information about the local symmetry in which the ion sits in its valence state, its site preference and determination of the degree of covalency of the metal-ligand bond. When a transition metal ion is embedded in a glass it need not have a centre of symmetry. This leads to mixing of d- and p- orbitals of the ion and, therefore, an electronic transition involves some charge transfer from a d-orbital to a p-orbital leading to weak absorption bands. If an ion is at the centre of symmetry, such a mixing does not occur but during the inevitable molecular vibrations make an ion spend part of the time away from the equilibrium position, which enables mixing of d- and p-orbitals and allow such transitions.
Most of the physical properties of the transition metal complexes are studied with the help of crystal field, ligand field and molecular orbital theories. The ligand field theory explains the optical levels by energy splitting of the states of the central ion in the field of the surrounding atoms. The theory of this splitting under the influence of fields produced by various symmetries was worked out by Bethe [53] and further developed by Schlapp and Penny [54], Van Vleck [55] and others.

The principal symmetry of the transition metal complexes is usually an octahedral one while in a few cases, tetrahedral, square planar and lower symmetries occur. In a complex the site symmetry of anions is always degraded from the extremely high spherical one to a lower symmetry. Two types of symmetries, known as octahedral (designated by $O_h$) and tetrahedral (designated by $T_d$) are important. The corresponding molecular structures having these symmetries are shown diagrammatically in Fig. 1.4.

Fig. 1.4 (a) Regular Octahedron point group ($O_h$)  
(b) Regular Tetrahedron point group ($T_d$)
A free d-electron has five-fold degeneracy with all the five d-orbitals, namely $d_{xy}$, $d_{yz}$, $d_{zx}$, $d_{x^2-y^2}$ and $d_{z^2}$ possessing the same energy (Fig. 1.5(a)). In a weak field approach, one tries to understand the effect of crystal fields on the free ion terms (Fig. 1.5 b, c, d).

![Fig. 1.5 (a) Five d orbitals of T$_{2g}$ orbitals and e$_{g}$ orbitals.](image)
Fig. 1.5 (b) Detailed spectral information on various transition metal (from $d^1$ to $d^4$) ions.
Fig. 1.5 (c) Detailed spectral information on various transition metal (from $d^6$ to $d^9$) ions.
Fig. 1.5 (d) Energy spectra of transition metal ions.
In weak field approach, one tries to understand the effect of crystal field on the free ion terms. For d, the application of the group theory results in the splitting of $^2\text{D}$ state into $e_g$ and $t_{2g}$ representations in octahedral crystal field. The crystal field potential acting on the ion is given by

$$V_{\text{oct}} = D(x^4+y^4+x^4-(3/5)r^4)$$

(1.5)

Where $D = (Ze/4a^5)$. This potential has to be applied on the wave functions which transform as $t_{2g}$ whereas $d_{x^2-y^2}$ and $d_{z^2}$ transform as $e_g$, and

$$<t_{2g}/V_{\text{oct}}/t_{2g}> = -4D_q$$

(1.6)

$$<e_g/V_{\text{oct}}/e_g> = 6D_q$$

(1.7)

Thus, the separation to $D_q$ between $t_{2g}$ and $e_g$ levels is a measure of the crystal field. The centre of gravity of the levels is preserved after application of the crystal field potential.

In $T_d$ symmetry the nature of the splitting is the same but ordering of the levels is inverted as shown in Fig. 1.6. If the symmetry is lower than octahedral, say tetragonal or orthorhombic, then these levels will split into levels of lesser degeneracy. The above discussion is valid for single electron d orbitals. Similar procedure is adopted for multi electron system where the terms will be split into various irreducible representations.

In the case of strong octahedral crystal fields, the single electron $t_{2g}$ and $e_g$ functions become the basis. The various configurations many electron systems are obtained by filling the $t_{2g}$ shell first and then the $e_g$ shell. Thus for example,
the d² ion has t_{2g}², t_{2g}¹, e_g¹ and e_g² configurations with energies - 8D_q, 2D_q and 12D_q, respectively.

**Fig. 1.6** Diagram showing relative energy of e_g and T_{2g} orbitals resulting from the splitting of d orbitals by octahedral environments.

The electrostatic energy values for different states have been calculated by Tanabe and Sugano [56] and Griffith [57] and they are presented these energy values in the form of matrices. For convenient interpretation of the observed optical spectra, Tanabe and Sugano have drawn energy level diagrams between E/B and D_q/B for various d^n configurations known as Tanabe-Sugano diagrams. Here, E corresponds to the energy level of a d^n system and B is the Racah inter-electronic repulsion parameter. These diagrams are mainly used in crystal field spectroscopy to evaluate the crystal field parameter D_q and parameters B and C. From these diagrams, it is possible to obtain a quantitative measure of the ease of spin pairing. These diagrams also help in assigning the transitions correctly.
1.2.3 Electron spin resonance

Electron spin resonance (ESR) has been developed as an extremely sensitive and important spectroscopy technique, which is widely used to study systems having unpaired electrons. In condensed matter physics, ESR is used as a powerful technique to study the lowest energy levels, hence, the electronic state of the unpaired electrons of paramagnetic species in solids. This technique provides information on understanding of the symmetry of the surroundings of the paramagnetic ion and the nature of its bonding to the nearest diamagnetic neighbours. Following are a few examples of systems containing unpaired electrons.

1. Atoms having odd number of electrons, e.g., atomic hydrogen and lithium atom.
2. Molecules with odd number of electrons such as NO, and triplet state molecules like oxygen molecule.
3. Ions having partially filled inner electronic shells, e.g., iron, rare earth ions etc.
4. Defects produced in a solid by irradiation.
5. Free radicals, e.g., CH₃ and diphenyl-picrylhydrazyl.
6. Conduction electrons in metals, semiconductors and dilute alloys etc.
When a system having non-zero angular momentum and magnetic moment is placed in an external magnetic field, each degenerate electronic level splits into a number of levels depending upon the value of angular momentum (Zeeman splitting). The ESR technique, basically, is the observation of the transitions induced by an electromagnetic radiation of appropriate polarization and energy (frequency) between these Zeeman levels. The energy separation of these levels is typically of the order of 1 cm\(^{-1}\) (microwave frequency range) in atomic and molecular systems. Thus, a microwave spectrometer is normally required to observe ESR.

An electron possesses spin and associated with it is the spin angular momentum “S” in units of ħ. An electron in a system like an atom or ion will also have, in general, an angular momentum “L” in units of ħ. The total angular momentum “J” is then given by

\[ \vec{J} = \vec{L} + \vec{S}. \]  

(1.8)

Associated with the total angular momentum J, the magnetic dipole moment \( \mu \) given by

\[ \vec{\mu} = -g \beta \vec{J}. \]  

(1.9)

where

\[ g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \]  

(1.10)

which is known as the Lande splitting factor for free ion and

\[ \beta = \frac{e\hbar}{2mc} = 9.274096 \times 10^{-27} \text{ erg/gauss} \]  

(1.11)
which is known as the Bohr magneton. When a magnetic dipole is placed in a uniform magnetic field $H$, it precesses about the direction of $H$ with the Larmor angular frequency $\omega_L$ which is given by [58]

$$\omega_L = \gamma B$$

(1.12)

where $\gamma = g \beta / \hbar$ is known as gyromagnetic ratio. Thus, the resonance condition will be satisfied only when the frequency of the incident radiation is given by

$$h = g \beta B.$$  

(1.13)

When an electromagnetic radiation of a frequency $\nu$ is applied to the sample, the resonant absorption of the energy by the unpaired electrons in the sample takes place whenever the resonance condition is satisfied.

The energy level of an electron with total angular momentum $J$ has a degeneracy of $(2J + 1)$. The application of an external magnetic field removes this degeneracy and the energy level splits into $(2J + 1)$ levels. When angular momentum $L$ is zero then $J$ becomes equal to $S$. The transitions between these levels are governed by the selection rules $\Delta M_s = \pm 1$, where $M_s$ is the spin magnetic quantum number. An unpaired electron with $S = \pm 1/2$, when placed in a uniform magnetic field $B$, will have two energy levels, as shown in Fig. 1.7, if $g$ is constant. The energies of these levels are
The magnetic dipole transitions between the levels are induced between the two levels in the presence of a uniform magnetic field $B$ and an alternating magnetic field polarized perpendicular to $B$ by an incident radiation of frequency $\nu$ if the quantum condition (1.13) and $\Delta M_s = \pm 1$ are satisfied. This will give rise to only one absorption line. When the orbital angular momentum is not zero then the degenerate energy level will split into $(2J+1)$ levels and the conditions for the transitions by absorption of energy is given by eqn. (1.13) and $\Delta M_J = \pm 1$. Such a situation will give rise to multiple absorption lines. The resonance
condition (1.13) can be satisfied either by changing the magnetic field or the frequency of the radiation incident on the magnetic dipole. Practically, it is more convenient to vary the uniform magnetic field rather than the frequency of the incident radiation since the frequency variation of a microwave source is possible within a very small range only.

Thus, from an ESR spectrum recording one can get information about the resonance field at a fixed frequency of the electromagnetic radiation, hence, the ‘g’ value, the shape, amplitude and width of the absorption line. The ‘g’ value may be modified by the crystal field surrounding the free ion from the value of the “free ion value”. All of these parameters, when interpreted properly and in conjunction with the appropriate theoretical ideas, provide valuable information on the system studied. In addition, one may vary certain other external parameters like temperature, composition etc., which would possibly change ESR parameters leading to additional information on the system under study. A vast discussion on ESR technique and its applications is available in a number of pioneering books written by many authors [59–63].

a) General Spin- Hamiltonian

In ESR spectroscopy, the transitions can be observed between the energy levels of ground state. In order to get the eigen values and eigen functions, we need to solve the Schrödinger’s time-dependent equation applied on Hamiltonian operator. For a Hamiltonian consisting of more than one term, the easier way to solve the equation is by perturbation theory. Here the eigen value is found by taking the strongest interaction and then the next interaction
will be treated as a perturbation of the levels obtained in the first case. This procedure is repeated until the weakest interaction is included. This method suffers with a draw back that various interactions should differ from one another by at least one or two orders of magnitude. Incidentally, this condition is satisfied in EPR spectroscopy.

The Hamiltonian, which describes various interactions of unpaired electrons with the static magnetic field and that of the surrounding environment, can be formalized in terms of spin operators. The coefficient of spin operators is called spin-Hamiltonian parameters.

The concept of Hamiltonian was originally developed by Pryce [64] and Abragam and Pryce [65] to interpret the observed resonance of ions in the first transition series. The concept was subsequently extended by Elliott and Stevens [66] to interpret the paramagnetic behaviour observed for the rare earth ions. The terms in the general Hamiltonian for an ion in a crystalline environment can be written as [67].

\[
H = H_E + H_{LS} + H_{SI} + H_Q + H_V + H_{SH} + H_{IH} \tag{1.16}
\]

Where the symbols indicate the type of interaction to which Hamiltonian applies and have the following meaning.

\(H_E\) is a composite term expressing the total energy of electrons, the columbic attractions of the electrons and the nuclei and the repulsion among the electrons

\[
H_E = \sum_i \left[ \frac{p_i^2}{2m} - \frac{Ze_i^2}{r_i} \right] + \sum_{ij} \frac{e^2}{r_{ij}} \tag{1.17}
\]
Where \( P_i \) is the momentum of the \( i^{\text{th}} \) electron, \( r_i \) is the distance of the electron from the nucleus, \( r_{ij} \) is the distance between the \( i^{\text{th}} \) electron and \( j^{\text{th}} \) electron and \( Z_e \) is the nuclear charge.

These terms are summed over all the electrons and yield the unperturbed electronic levels before considering the interaction between spin and orbital angular momenta. The separations will be of the order \( 10^5 \text{ cm}^{-1} \).

\section*{ii.} \( H_{LS} \) represents the spin-orbit coupling and may be written in the form.

\[
H_{LS} = \sum \lambda_{ij} \cdot l_i \cdot s
\]  

(1.18)

Where \( l \) is the orbital angular momentum of the individual electron, ‘s’ is the spin angular momentum of the individual electron and \( \lambda_{ij} \) is the spin–orbit coupling constant. This can be written in a simple form as

\[
H_{LS} = \lambda \cdot L \cdot S
\]  

(1.19)

Where, \( L \) and \( S \) are the total orbital angular momentum and the spin angular momentum of free ion respectively. The magnitude of this interaction lies in the range \( 10^2 \) to \( 10^3 \text{ cm}^{-1} \).

\section*{iii.} \( H_{SI} \) describes the magnetic interaction between each electron and the nucleus

\[
H_{SI} = \sum a_i \cdot J_i \cdot I_i
\]  

(1.20)

Where \( J_i \) is the total angular momentum of the \( i^{\text{th}} \) electron and \( I_i \) is the nuclear spin. The magnitude of this interaction will be of the order of \( 10^{-2} \text{ cm}^{-1} \).

\section*{iv.} \( H_Q \) represents the nuclear quadrupole interactions, which are even smaller than \( H_{SI} (\sim 10^{-4} \text{ cm}^{-1}) \) and may be neglected. For nuclei with spin \( I > \frac{1}{2} \), these interactions shift the hyperfine levels by a small amount.
\[ H_0 = \sum I_i \cdot Q_i \cdot I_i \quad (1.21) \]

\[ H_v = \sum e_i \mathbf{V}(r_i) \quad (1.22) \]

\( v. \) \( H_v \) represents the effect of crystal field, which can be written as

Where \( \mathbf{V}(r_i) \) is the electrostatic potential at the ion with which each electron interacts.

In an external magnetic field \( B \), the terms \( H_{SH} \) and \( H_{IH} \) must be added to represent the interaction of the angular momentum of electrons and nuclei respectively with the magnetic field.

\[ H_{SH} = \beta \left( \mathbf{L} + g_e \mathbf{S} \right) \cdot \mathbf{B} \quad (1.23) \]

\[ H_{IH} = \hbar / 2 \pi \sum_i -\gamma_i \cdot I_i \cdot \mathbf{B} \quad (1.24) \]

Where \( \gamma_i \) is the gyrometric ratio of the \( i^{th} \) nucleus and the latter terms (about \( 10^{-4} \) cm\(^{-1}\)) may be neglected except in considering second order effects in the nuclear hyperfine interaction.

**b) Line shapes**

The most commonly observed shape functions in EPR spectroscopy are Lorentzian and Gaussian, described by the functions given below.

\[ I = \frac{I_0}{T_2^2(B-B_r)^2+1} \quad (1.25) \]

\[ I = I_0 \exp \left[-b(B-B_r)^2T_2^2\right] \quad (1.26) \]

Where \( I_0 \) is the intensity of the absorption at its centre, \( B_r \) is the resonant field at the line centre. The constants \( T_2^2 \) and \( b \) are related to the half width of each of the two types of curves.
The Lorentzian shape arises due to harmonically bound electron. If the harmonic motion of the electron is interrupted by some process, then the distribution of frequencies follow the eqn. (1.26) for an EPR spectrum, the interruption will be in the form of exchange. Since all the electrons are equivalent, their interchanging between two molecules is quite possible if the molecules are close enough to each other. If this exchange is so rapid to affect the phase coherence of the spins, Lorentzian shape results.

On the other hand, Gaussian shape results from the paramagnetic ion separated from each other by molecules, which are having no unpaired electrons but possessing magnetic nuclei. Each unpaired electron will experience a local static magnetic field which will be dominated by how the nuclear spins are arranged in the near by host molecules. The observed EPR spectra will be a superposition of shapes from all the spins with their local fields. Since the local fields will be randomly distributed, the total line shape results in a Gaussian line shape according to equation (1.25). The characteristic Lorentzian and Gaussian line shape are shown in the Fig. 1.8.

c) Line Width and Intensities

Generally the EPR signals are recorded as the first derivative of the absorption curve and hence the area under the EPR signal can be calculated by numerical double integration method. In this method, the EPR spectrum is divided in to ‘n’ small intervals having length ‘d’.
The height $h_r$ of the EPR signal corresponding to the centre of $r^{th}$ interval is noted and the area under the curve can be calculated from the equation

$$ A = \frac{1}{2} d^2 \sum_{r=1}^{n} (n - 2r + 1) h_r \quad (1.27) $$

Fig. 1.9 shows the method of finding the area under the first derivative absorption curve by numerical double integration method. The accuracy of this method depends on the number of intervals and complexity of the spectrum. Using about 8 to 10 intervals per peak, the error in calculating the area will likely be within 2 to 3% in Gaussian curves. For Lorentzian curves, the error may be greater due to the presence of long tails.
For ESR signals, the line widths are measured from the maximum and minimum line positions at the first derivative curve. The ESR lines always have a finite width due to electrons interacting magnetically with the environment of the sample. Hence, from the line width and the rate of build up or decay of the line intensity, one can obtain information about spin environment.

The intensity of ESR signals depends on various factors (1) Concentration of the paramagnetic ion (2) the microwave frequency (3) the power of micro waves (4) the transition probability and (5) the temperature.

Fig. 1.9 The method of finding the area under the first derivative absorption curve by numerical double integration method.
1.2.4 Infrared spectra

Infrared absorption spectra of glasses can provide significant and valuable information on the arrangement of atoms, nature of chemical bonding between them, the changes in the atomic configurations caused by increase of decrease of concentration of glass-forming systems and in general, facilitate the probing of the short- and intermediate range in glass networks.

In addition, the investigation of infrared spectra (IR) of glasses enables the assignment of characteristic frequencies to molecular groups in the glass and hence correlation of IR absorption bands with different units of vitreous structure. In the case of phosphate glasses, the basic glass contains PO$_3$, PO$_4$ structural units in the phosphate glass network and when a cation such as Y$^+$ or La$^+$ or Sc$^+$ is added, it may reside interstitially. Such information about the changes in the basic glass structure that take place upon the addition of a cation can also be studied from the IR spectra.

The vibrations of structural units in a glass are independent [68–70], unlike the vibrations of complex ions in a crystalline matrix which are dependent of the vibrations of other groups. In probing the structural units and changes that take place in the network with composition of a ternary glass, infrared spectroscopy lends itself as an effective tool, because the technique is sensitive to short-range ordering and local interactions.

The assignment of the important IR bands observed in transition metal ions doped (MoO$_3$, Cr$_2$O$_3$, WO$_3$), PbO–Y$_2$O$_3$–P$_2$O$_5$, PbO–La$_2$O$_3$–P$_2$O$_5$, PbO–Sc$_2$O$_3$–P$_2$O$_5$ glasses of the present work is in general made by comparison of
the data with the bands observed in literature, even though some bands attributions have their support from the theory. However, it is possible to provide quantitative justification from the theoretical calculation in the literature [71] for some of the vibrational frequencies assigned to phosphate, molybdate and other transitional ion groups. Such justification could have been offered even for the IR spectrum observed for MoO$_3$, Cr$_2$O$_3$ and WO$_3$ provided the force constant corresponding to Mo–O, Cr–O and W–O stretchings are known.

When the characteristic group frequencies arise from the vibrations of pure stretching character or of pure bending nature the wavenumber $\bar{\nu}$ is given by the equation

$$\bar{\nu} = \frac{1}{2\pi c} \left( \frac{K}{\mu} \right)^{1/2}$$

(1.28)

where $c$ is the velocity of light, $m$ is the reduced mass of the diatomic or triatomic group, $K$ is the stretching or bending force constant. For certain diatomic and triatomic groups, the force constant was evaluated using various empirical formulae available in the literature [71, 72].

1.3 Brief review of the recent work on lead phosphate glasses

Yasser B. Saddeek et al [73] prepared La$_2$O$_3$–PbO–Al$_2$O$_3$–P$_2$O$_5$ glasses and their structures were studied by FTIR. The physical parameters such as the density, the dimensionality and the elastic moduli of the phosphate network are sensitive to the concentration of Al$_2$O$_3$. The elastic moduli were calculated in terms of Makishima–Mackenzie model. The results of the density and the elastic moduli were interpreted in terms of the vibrations of aluminates and
phosphate structural units and the replacement of low bond strength PbO by high bond strength Al₂O₃. Ivana Rosslerova et al [74] studied crystallization of PbO–WO₃–P₂O₅ glasses by thermo analytical and spectroscopic methods. Raman spectra of the crystallized samples confirmed the results of the X-ray diffraction measurements and provided information on the thermal stability of the glasses and formation of the glass-crystalline phases by the annealing of glass samples. M. Soltys et al [75] prepared Lead phosphate glasses singly doped with Dy³⁺ ions were studied. Local structures were examined using FT-IR. Excitation and luminescence spectra for Dy³⁺ ions in investigated lead phosphate glasses were registered. Luminescence intensity ratio Y/B related to ⁴F⁹/₂→⁶H⁷/₂ (where J=15, 13) transitions was determined and luminescence lifetime (τ_m) for the ⁴F⁹/₂ state of Dy³⁺ ions were also measured. Ravneet Kaur et al [76] have been studied PbO–Na₂O–B₂O₃–SiO₂ glasses using the melt quenching technique. The structural properties of these glasses have been investigated using the FTIR spectroscopy. The effect of the presence of modifier PbO on the glass system is also studied. The FTIR spectral investigation of these glasses exhibits characteristic vibrations of BO₄ and BO₃ units together with SiO₄ as well as PbOₙ (n=4,6) groups. The gamma ray interaction of the present glass system in the dose range 0.1–60kGy is investigated. U. Hoppe et al [77] have studied Na₂O–SiO₂–P₂O₅ glasses with large P₂O₅ contents, and the structures of these glasses with similar P₂O₅ contents. This behavior is investigated by X-ray and neutron diffraction. P. Ramesh Babu et al [78] studied the influence of In₂O₃ on electrical
characteristics of iron mixed Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$ multi-component glass system were synthesized. Dielectric properties, optical absorption and ESR spectra have revealed. Xiuying Li et al [79] studied ZnO–Fe$_2$O$_3$–P$_2$O$_5$ glass series and investigated by Raman and IR spectral changes with increasing O/P ratio from 2.8 to 3.7 were summarized. Spectral changes mainly include relative amplitudes decrease of Raman bands at ~1344, ~1205 and ~705 cm$^{-1}$, relative amplitudes increase of Raman bands at ~947 and ~1080 cm$^{-1}$, intensification of the overlaps of IR absorption bands in the region of 900–1400 cm$^{-1}$, obvious decrease in relative amplitudes of IR bands at ~1351, ~1251, ~780 and ~480 cm$^{-1}$ and the shift of the band at ~480 cm$^{-1}$ to higher wave number. These spectral changes have shown a gradual depolymerization of phosphate network and the variation of dominant structural units from Q$^2$ to Q$^1$ species with increasing O/P ratio from 2.8 to 3.7. Yasser B.Saddeek et al [80] have been prepared and characterized Al$_2$O$_3$–La$_2$O$_3$–P$_2$O$_5$–PbO glasses. The physical parameters such as the density, the dimensionality and the elastic moduli of the phosphate network are observed sensitive to the concentration of Al$_2$O$_3$. The elastic moduli were calculated in terms of Makishima–Mackenzie model. The results of the density and the elastic moduli were interpreted in terms of the vibrations of aluminates and phosphate structural units and the replacement of low bond strength PbO by high bond strength Al$_2$O$_3$. D.A.Magdas et al [81] studied the structure of CuO.[P$_2$O$_5$–PbO] glasses. Raman spectrum was made in order to make a better identification and assignment of all bands which appear in these spectra. By adding CuO, the
symmetric vibration of P–O–P bond in \( Q^2 \) groups shifts to higher frequencies due to the depolymerization of long phosphate chains and the bands attributed to \((PO_2)_{\text{asym}}\) stretching and \((P=O)_{\text{sym}}\). Stretching vibrations shift to lower frequencies due to the linking of P–O bond to cooper ions. Khamirul Amin Matori et al [82] studied series of binary \((\text{PbO})_x(\text{P}_2\text{O}_5)_{1-x}\) lead phosphate glasses with various mole fractions \((x=0.1\) to 0.6\) was carried out using a conventional melt-quenching method. The ultrasonic wave velocities \((V_1\) and \(V_t\)) of the glasses were determined at room temperature by using a non destructive test. The experimental data for the were then used to determine the elastic properties in each series of lead phosphate glass systems: the longitudinal, shear, bulk and Young's moduli; Poisson's ratio; and the Debye temperature. Based on the results wave velocities and densities obtained, the longitudinal, shear, bulk and Young's moduli of the glasses increased with the addition of PbO content. Hassan ElHafi et al [83] have been prepared and characterized the magnetic properties of \(\text{PbO–Fe}_2\text{O}_3–\text{P}_2\text{O}_5\) glass system. Magnetization, magnetic susceptibility and specific heat measurements carried out on \(\text{PbFe}_3\text{O}(\text{PO}_4)_3\) powders firmly establisha series of three ferromagnetic \((\text{FM})–\text{like second order phase transitions spanned over the 32–8 K temperature range. A first extraction of the critical exponents } (\beta, \gamma, \delta) \text{ was performed by ac magnetic susceptibility in both } \text{PbFe}_3\text{O}(\text{PO}_4)_3 \text{ powders and single crystals and the values were found to be consistent with mean-field theory.} \)
N.A.Ghoneim *et al* [84] prepared and characterized Pristine lithium phosphate, lead phosphate and zinc phosphate glasses, the UV–visible and infrared absorption spectra of the prepared samples were measured before and after gamma irradiation. Optical spectra of these prepared glasses reveal strong UV absorption bands. The effects of gamma irradiation on the IR spectra are limited to a slight decrease of the intensities for some IR bands. The IR spectra are observed to be slightly affected by the increase of TiO$_2$ indicating the stability of the main phosphate network units and the shielding behavior of titanium ions. G.Upender *et al* [85] studied Li$_2$O–P$_2$O$_5$–TeO$_2$–CuO glasses. The glass transition temperature ($T_g$) of glass samples have been estimated from DSC traces and found that the $T_g$ increases with increasing P$_2$O$_5$ content. Both the IR and Raman studies have been showed that the present glass system consists of [TeO$_3$], [TeO$_4$], [PO$_3$] and [PO$_4$] units. N.Vedeanu *et al* [86] synthesized and characterized addition of copper oxide to lead–phosphate glasses by EPR and IR spectroscopy. IR spectra shows the shift of P–O asymmetric stretching vibration band to lower wave number can be explained by the increase of PO$_4$ tetrahedra charge density leading a more ionic and less covalent bonding. R.Lakshmikantha *et al* [87] have been prepared and characterized the lithium doped lead zinc phosphate glass system. Thermal stability factor (S) has been evaluated using the values of $T_g$ and $T_c$. The refractive indices of these glasses lie in the range of 1.40–1.45. IR spectra of these glasses show absorption peaks in the range 1233–1247 cm$^{-1}$, 1076–1087
cm$^{-1}$, 905–894 cm$^{-1}$, 735–731 cm$^{-1}$ and 531–556 cm$^{-1}$ corresponding to P =O, P–O’, (P–O–P)$_{AS}$, (P–O–P)$_{S}$ and O–P–O vibrations respectively.

Ch. Srinivasa Rao et al [88] have been prepared Ho$^{3+}$-doped P$_2$O$_5$–K$_2$O–Al$_2$O$_3$–PbO–Na$_2$O–Ho$_2$O$_3$ glasses. The optical properties have been characterized through absorption, emission and gain spectra and decay rate analysis. A strong dependence of the $\Omega_2$ parameter on the hypersensitive transition has been noticed. Using the Judd-Ofelt intensity parameters, various radiative properties like transition probabilities, branching ratios and radiative lifetimes for various emission levels has been evaluated. N.S. Vedeanu et al [89] have studied influence of some transition metal ions in lead- and calcium-phosphate glasses. The structural study on some phosphate glasses containing vanadium, copper, molybdenum and iron ions were investigated by EPR method. Ladislav Koudelka et al [90] studied PbO–MoO$_3$–P$_2$O$_5$ glasses by Raman and NMR spectroscopy. They reported glass transition temperature increases with increasing MoO$_3$ content having a maximum at x=50 mol% MoO$_3$. The analysis of Raman spectra of glasses with a high MoO$_3$ content showed the transformation of octahedral MoO$_6$ units into tetrahedral MoO$_4$ units. C. Ivascu et al [91] prepared and investigated the P$_2$O$_5$–BaO–Li$_2$O glasses. The predominant absorption band from IR spectra is attributed to the symmetric stretching vibrations of P=O double bonds. Raman spectra of the studied glasses contain also typical phosphate glasses bands. FT-IR and Raman spectroscopies revealed a local network structure mainly based on Q$^2$ and Q$^3$ tetrahedrons connected by P–O–P linkages. Luminescence investigations show
that by adding modifier oxides to phosphate glass dose dependent TL signals result upon irradiation. E.Mansour et al [92] prepared ZnO-PbO-P2O5 glasses and investigated FTIR, density, molar volume (V_m), and DC conductivity. Both density and molar volume decreases systematically with composition. FTIR analysis indicates that ≥ 30mol% (PbO and/or ZnO) enters the glass structure as formers. Below and above that concentration a decreasing amount of Pb^{2+} (Zn^{2+}) is incorporated into the network as modifier. B.Eraiah et al [93] studied lead-phosphate glasses doped with samarium trioxide, by using conventional melt quenching method and their elastic properties have been studied at room temperature. The longitudinal and transverse sound velocities decrease by increasing the Sm_2O_3 content. Elastic moduli, Poisson’s ratios decrease with increase of Sm_2O_3 composition up to 0.3mol% and then there is a slight increasing trend observed at 0.4mol%. M.V.N.Padma Rao et al [94] prepared the PbO–CaF_2–P_2O_5 glasses containing small concentrations of CuO and investigated dielectric studies, infrared, optical absorption ESR and photoluminescence spectra. L.M.Sharaf El-Deen et al [95] investigated spectral properties of PbO–P_2O_5 glasses. The spectral absorption of these glasses was measured in the spectral range 300–900 nm at room temperature. Optical absorption spectra show that the absorption edge has a tail extending towards lower energies. The edge shifts nearly linearly towards higher energies with increasing PbO content. The optical energy gap increases, from 2.55 to 3.05 eV by increasing PbO content from 5 to 30 mol%. The width of the localized states is decreased by increasing PbO content. Marcin Sobczyk et al [96] studied
46PbO:53P_2O_5:Ln_2O_3 glasses, where Ln = Sm or 0.1 Sm +0.9 Gd. The luminescence branching ratios and quantum yields have been computed using the Judd–Ofelt analysis of relevant absorption spectra and the observed luminescence lifetimes. R.Praveena et al. [97] have been characterized fluorescence spectroscopy of Sm^{3+} doped lead phosphate based glasses modified with niobium and characterised an optical absorption, emission spectra and decay curve analysis.

D.A.Magdas et al. [98] studied the xFe_2O_3(1-x)[2P_2O_5PbO] glasses system with 0 ≤ x ≤ 50 mol%. The addition of iron oxide leads to more P=O bond breakage and the formation of the P–O–Fe bonds. Concluded that at high content of Fe_2O_3 it acts in the structure of glasses as a network former. The presence of the Fe–O–P bonds for higher content of iron oxide in this glass system is consistent with the improving of their chemical durability.

N.Krishna Mohan et al. [99] prepared PbO–Nb_2O_5–P_2O_5–MnO glasses and investigated differential thermal analysis, infrared, optical absorption, luminescence, Raman and ESR spectra, magnetic susceptibility and dielectric properties. The results have been analyzed in the light of different oxidation states of manganese ions. G.Sahaya Baskaran et al. [100] prepared PbO–P_2O_5–As_2O_3–Ga_2O_3 glasses and studied dielectric properties, optical absorption, infrared and Raman spectra. J.Schwarz et al. [101] Measured optical gap (Eg) between 4.54 eV–4.88 eV at room temperature was determined for PbO–ZnO–P_2O_5 glasses with the content of P_2O_5 in the region of 30 to 50 mol% and with the content of PbO in the region of 50 to 45 mol%, respectively. The
temperature (T) dependence of the optical gap \( (E_g(T)) \) in the region 80K\[K\]b600 was determined, and an electron–phonon interaction is suggested to be a major contribution to the temperature shift of the optical gap. G. Sahaya Baskaran et al [102] have been studied PbO–P_2O_5–As_2O_3 glasses containing different concentrations of In_2O_3 glasses. Chemical durability, differential thermal analysis, infrared, optical absorption and Raman spectra, and dielectric have been carried out. The studies of dielectric properties reveal that the presence of indium oxide in the glass network causes a considerable improvement in the insulating strength of the lead phosphate glasses. N. Krishna Mohan et al [103] prepared PbO–Nb_2O_5–P_2O_5–Fe_2O glasses and studied chemical durability, differential thermal analysis, infrared, optical absorption ESR spectra and dielectric studies. The analysis indicates that the iron ions exist mostly in trivalent state and occupy both tetrahedral and octahedral substitutional positions and are found to increase the rigidity of the glass network.

O. Cozar et al [104] studied structure of xWO_3·(100–x)[2P_2O_5·PbO] and xMoO_3·(100–x)[2P_2O_5·PbO] glass systems with 0\( \leq x \leq 50 \) mol% is investigated by IR, Raman and EPR spectroscopy. The characteristic absorption bands of these glasses due to the stretching and bending vibrations are identified and analyzed by the increasing of molybdenum and tungsten oxides content. EPR data shows that for \( x \leq 10 \) mol% the isolated Mo^{5+} and W^{5+} ions prevail in a square–pyramidal form (C_{4v}) and rhombic symmetry respectively. At high MoO_3 content \( (x > 20 \) mol%) the dipole–dipole and super
exchange coupled Mo\(^{5+}\) ions appear. This fact does not occur in case of W\(^{5+}\) ions because of their small number. S.V.G.V.A.Prasad et al [105] studied BaO–Al\(_2\)O\(_3\)–P\(_2\)O\(_5\) glasses containing different concentrations of NiO. A number of studies viz., chemical durability, differential thermal analysis, infrared, optical absorption spectra, magnetic susceptibility and dielectric properties of these glasses have been carried out. The studies on chemical durability indicate that there is a significant increase in the corrosion resistance of the glasses; whereas the results of differential thermal analysis suggests that there is a substantial improvement in the glass forming ability, with increase in the concentration of NiO up to 0.6 mol\% in the glass matrix. The optical absorption, magnetic susceptibility and IR spectral studies point out nickel ions occupy both tetrahedral and octahedral positions in the glass network. Takeba et al [106] have carried out the studies on dissolution behaviour of zinc phosphate glasses in water. Saranti et al [107] have reported preparation structural study and vitro evaluation of calcium borophosphate bioactive glass system. Datta et al [108] have reported the influence of manganese and vanadium ions on the physical properties of phosphate glasses. Agathopoulos et al [109] have reported the results of their study on the structural analysis and devitrification of calcium silicate glasses with P\(_2\)O\(_5\) as additive. Gracal et al [110] have investigated the electric behaviour of lithium niobium phosphate glasses and glass ceramics. In their study they have found that there exists a relation between the number of lithium niobate ferroelectric crystals present in the glass ceramics and dielectric constant. Ahmed et al [111] have reported the
thermo dynamics of ions exchange of alkali metal ions on crystalline niobium phosphate using Gaines-Thomas equation. Rambo et al [112] have recently described the methods of manufacturing of porous niobium phosphate glasses. From this study, they have concluded that these porous niobium phosphate glasses are potential candidates for immobilization of liquid nuclear waste. Simon et al [113, 114] have reported the results on their studies on thermal and structural investigations on niobium phosphate glasses that are useful for biomedical applications. Datta et al [115] have reported the effect of mixed transition –metal ions (vanadium and iron) in phosphate glasses.

Jozwiak and Garbarczyk et al [116] have reported the mixed electronic – ionic conductivity in the lithium phosphate glasses mixed with V₂O₅. Datta et al [117] have carried out the influence of iron and manganese ions on the properties of phosphate glasses. Gafrarczyk and Wasiucionek et al [118] have investigated the electrical properties and crystallization process of silver phosphate glasses. Guo et al [119] have reported that niobium phosphate glasses to have a large bandwidth for Raman gain applications. H. Doweidar et al [120] have been studied Infrared spectra of Fe₂O₃–PbO–P₂O₅ glasses. Measured intensity and frequency of the IR bands and structural groups in the glass matrix. They reported spectral analyses revealed that the short-range order of the glassy matrix is strongly affected by the addition of PbO and/or Fe₂O₃ to P₂O₅ glass. The changes observed in IR spectra of PbO–P₂O₅ glasses are related to the dual role of lead ions as a glass former and modifier. The results revealed that there are critical concentrations of Fe₂O₃ at which iron ions change their
local structure. C. Dayanand et al [121] studied Thermal (DSC) characterization of xPbO–(1−x) P₂O₅ glass system. They prepared lead phosphate (LP), xPbO–(1−x) P₂O₅ glasses, divided into three compositional regions, x=0.3–0.5 (region I), x = 0.55–0.6 (region II), and x=0.66–0.75 (region III) were prepared by single-step melt-quenching process with the melt-temperature increasing from 550 to 750 °C. The DSC studies reports two endotherm peaks. The first and weak endotherm around 130 °C has been attributed to a thermal event in which dehydration of glasses takes place. The second and stronger endotherm has been attributed to the glass transition (T_g) phenomenon. The onset of the glass transition temperature was found to increase from about 212 °C for the glass sample with x=0.3 to about 345 °C for the glass with x=0.6 in the compositional region II where both crystalline and glass phase co-exist. The observed splitting in the endotherms of glasses in the region II co-relates well with the mixed phase. V. Sudarsan et al [122] studied thermal and structural studies on TeO₂ substituted (PbO)₀.₅(P₂O₅)₀.₅ glasses. (PbO)₀.₅₀(P₂O₅)₀.₅₀₋ₓ(TeO₂)ₓ and (PbO)₀.₅₀₋₀ₓ(P₂O₅)₀.₅₀(TeO₂)₀ₓ glasses with 0.0 ≤ x ≤ 0.2 and 0.0 ≤ y ≤ 0.2, and characterized by ³¹P magic angle spinning nuclear magnetic resonance (MAS NMR), Infrared (IR) and Differential Thermal Analysis (DTA) techniques. Rajendra et al [123] have studied the effect of thermal treatment on elastic properties of SiO₂–Na₂O–CaO–P₂O₅ glasses that are useful for biomedical applications. Ahamad et al [124] have reported the processing and characterization of ternary based sodium calcium phosphate glass system.
Nogami et al [125] has reported the results of their studies on proton conductivity in sol-gel-derived $\text{P}_2\text{O}_5$–$\text{TiO}_2$–$\text{SiO}_2$ glass system. Ghussn and Martinelli et al [126] have suggested a novel method to produce niobium phosphate glasses by microwave heating. Martinelli et al [127] have carried out a large number of studies on niobium barium phosphate, potassium barium phosphate glasses. Their studies include DTA, XRD, optical absorption, IR and Raman spectroscopy of these glasses. Sene et al [128] have carried out the structural investigations of rare earth doped niobium phosphate glasses. Mazalil et al [129] have reported their study on preparation and characterization on lithium Niobium calcium phosphate glasses. In their study it was revealed that the thermal expansion co-efficient and glass transition temperature are strongly dependent on the ratio of the concentration of $\text{Nb}_2\text{O}_5$ and $\text{P}_2\text{O}_5$ in the glass matrix. K. El-Egili et al [130] studied physical properties of $\text{PbO}$–$\text{P}_2\text{O}_5$ glasses investigated using IR spectroscopy and by means of density and electrical-resistivity measurements. The infrared spectra revealed that for $\text{PbO}<50$ mol% $\text{PbO}$ enters the structure as a network modifier forming non-bridging oxygen ions. The conductivity of these glasses depends mainly on the mobility of $\text{Pb}^{2+}$ ions. The variation of the electrical conductivity parameters upon changing the composition have been correlated with the structural changes in the glass matrix. C.G.S. Pillai et al [131] have been prepared $\text{PbO}$–$\text{P}_2\text{O}_5$ glasses in which part of $\text{PbO}$/$\text{P}_2\text{O}_5$ was replaced by $\text{ThO}_2$ structural aspects have been studied by $^{31}\text{P}$ MAS NMR, Raman and FTIR techniques. When part of the PbO has been replaced by $\text{ThO}_2$, the phosphorusst ructural units are not significantly
affected, indicating that Th$^{4+}$ replaces Pb$^{2+}$ at the interstitial positions in the
glass network. P. Subbalakshmi et al [132] prepared tungsten phosphate glasses
mixed with the three different modifier oxides, viz. PbO, ZnO and CaO doped
with Er$_2$O$_3$. 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. The Judd–Ofelt
theory could be successfully applied to characterise the absorption and
luminescence spectra of these glasses. The radiative properties like transition
probability A, branching ratio $\beta_r$, the radiative life time $\tau_R$, and the emission
cross-section $\sigma^E$ for various emission levels of these glasses have been
determined and reported. P. Subbalakshmi et al [133] studied dielectric
dispersion and certain other physical properties of PbO–Ga$_2$O$_3$–P$_2$O$_5$ glass
system. Investigated dielectric properties, dielectric breakdown strength,
optical absorption, IR spectra and elastic properties. Finally conclude that the
insulating and mechanical strength of the glasses is comparatively high when
Ga$_2$O$_3$ is present in small quantities (~5 mol%) in the glass matrix. Salagram et
al [134] reported about the optical band gap studies on Pb$_3$O$_4$–P$_2$O$_5$ lead (II, IV)
phosphate glasses. M. Abid et al [135] have studied thermal and electrical
properties of xLi$_2$O–(0.50-x) PbO–0.50P$_2$O$_5$ (0 ≤ x ≤ 0.50). DSC measurements
give the variation of $T_g$ from 395°C (for x =0) to 302°C (for x = 0.50). Ionic
conductivity increases from $2.23 \times 10^{-7}$ (for x =0.10) to $10^{-3} \Omega^{-1}.cm^{-1}$ (for x =0.50)
at 300°C; the activation energy decreases from 1.05 to 0.71 eV on increasing
lithium content.
Dongmei Zhu et al [136] prepared PbBr$_2$–PbCl$_2$–PbF$_2$–PbO–P$_2$O$_5$ glass melted at 450-470°C there was a remarkable difference between two factors. The incomplete decomposition of NH$_4$H$_2$PO$_4$ or the reaction between P$_2$O$_5$ and H$_2$O in the atmosphere increases the content of O, while the volatilization of P$_2$O$_5$ decreases the content of O. Richard et al [137] reviewed the spectroscopic and diffraction studies of simple phosphate glasses and structures of anhydrous ultra phosphate glasses. Ilieva et al [138] studied infrared and Raman spectra of Ga$_2$O$_3$–P$_2$O$_5$ glasses and concluded that the structure of these glasses is highly polymerized network. Sudarsan and Kulshreshtha et al [139] reported that Sb$_2$O$_3$ containing phosphate glasses were found to be thermally more stable compared to PbO–P$_2$O$_5$ glasses. Dongmei Zhu et al [140] have been prepared and characterized the PbBr$_2$–PbCl$_2$–PbF$_2$–PbO–P$_2$O$_5$ glass system results show that the PbBr$_2$–PbCl$_2$–P$_2$O$_5$ ternary system has a broad glass-forming region which extends to 30 mol% P$_2$O$_5$. Most of the glasses in this system show strong stability against crystallization and some have glass transition temperatures as low as 146°C. When 5% PbO or 5% PbF$_2$ is introduced into the PbBr$_2$–PbCl$_2$–P$_2$O$_5$ system, the glass-forming region becomes smaller and the glass transition temperatures increase. However, the introduction of 2.5% PbF$_2$ and 2.5% PbO into the ternary system increases the glass transition temperature and broadens the glass-forming region. Belkabir et al [141]. Na$_2$O–Ga$_2$O$_3$–P$_2$O$_5$ glasses are structurally characterized as a function of Na/Ga molar ratio. Andrade et al [142, 143] have investigated the Raman, infrared and Mossbauer spectra of potassium niobium phosphate glasses mixed
with iron oxide. Abd EL-ATI and Higazy et al [144] have studied the electrical conductivity and optical properties of gamma ray irradiated niobium phosphate glasses. They have analyzed the results of optical absorption in the light of indirect transition. Hongsheng Zhao et al [145] have been prepared and characterized PbO–PbBr$_2$–PbF$_2$–P$_2$O$_5$ glass system. The glass-forming regions have been explored and the stabilities of the glasses against crystallization studied. The composition, densities, characteristic temperatures, and the chemical stabilities against water of the glasses were measured. Most of the glasses in these two systems show strong stabilities against crystallization. Suzuya et al [146] studied the structures of lead indium phosphate and lead scandium phosphate and reported about the coordination numbers. Zhao et al [147] reported that most of the glasses in the PbO–PbBr$_2$–PbF$_2$–P$_2$O$_5$ system show strong stabilities against crystallization. Araujo et al [148] have reported the structure and nucleation mechanism of the iron lithium niobium phosphate glasses by means of infrared spectroscopy and DTA.

Aruna and Buddhudu et al [149] studied the spectral properties of Tb$^{3+}$:B$_2$O$_3$–P$_2$O$_5$–R$_2$SO$_4$ glasses (R=Li, Na, K) and they have found that this glass system to be green fluorescent ($\lambda_{exc} = 487$ nm). Hallori et al [150] studied optical and structural properties of Er$^{3+}$doped P$_2$O$_5$–SiO$_2$ and Al$_2$O$_3$–SiO$_2$ planar wave-guides. Sidek and Senin et al [151] investigated elastic and inelastic and non-liner acoustic properties of ZnCl$_2$–P$_2$O$_5$ glasses. Zhao et al [152] reported the synthesis of three Eu$^{3+}$ doped in B$_2$O$_3$–P$_2$O$_5$–R$_2$SO$_4$ (R=Li, Na, K) glass system; on excitation with 395 nm (Xe-arc lamp) these Eu$^{3+}$ glasses were found
to be red fluorescent and the richness of the red colour was high in Li$^+$ glass than the rest of the glasses. Meyer et al [153] analysed the characterization of the structure of binary zinc ultra phosphate glasses by IR and Raman spectroscopy. Liu et al [154] concluded that the length of phosphate chains decreases with increase in PbO and or ZnO contents in the glass matrix. Miklos and Doupovec et al [155] studied the dielectric properties of V$_2$O$_5$–P$_2$O$_5$ glasses and reported that the conductivity and dielectric properties of the glasses could be described by mechanism of electron hopping between energy states of the chain of molecules or by a tunneling effect. Rao et al [156] studied elastic properties of binary and ternary P$_2$O$_5$ glasses using ultrasonic measurements and reported that the variations in the moduli are consistent with the nature of the structural units formed at various compositions. Brow et al [157] examined the polyhedral arrangements in ZnO–P$_2$O$_5$ glasses using MAS-NMR spectroscopy and Raman spectroscopy. Quinn et al [158] concluded from their studies that zinc phosphate glasses are chemically durable and have processing temperatures under 400 °C and can be co-formed with high temperature polymers to produce unusual organic/inorganic composites. Angel et al [159] has reported the transition from cross-linked ultra phosphate structures to polymer like metaphosphate structure affects the temperature dependence of viscosities of alkali phosphate liquids; he also concluded that in general metaphosphate liquids are more fragile than ultra phosphate liquids. Ingram et al [160] reviewed the ionic conductivity in these glasses and suggested that it is related to the structural disorder in the form of the amorphous cluster theory.
Bunker et al [161] Average chain lengths of typical meta phosphate glasses, with $n_{av}$ ranging from 40-100 P-Tetrahedra and terminated by hydroxyl groups, had been reported. Gresch et al [162] analysed the spectral studies of Na-ultra phosphate glasses. Ray et al [163] studied the Raman spectra of K-ultra phosphate glasses.

1.4 Motivation and objective of the present work

Lead phosphate glass materials are expected to possess outstanding properties like high mechanical, electrical and thermal properties. These glasses have poor chemical durability and high thermal expansion coefficient have been the subject of many investigations on account of their catalytic properties. Phosphate glasses are declared as laser hosts and solid state ionic conductors. Recently, phosphate glasses have received a great deal of attention due to their potential application in optical data transmission, detection, sensing and laser technology, waveguide and fiber optical amplifier devices.

The characteristics of glass however depend on the kind and quantity of glass composition. Hence, the selection of a suitable constituents oxides and dopants in the correct concentration are important factors, in the formation of glass. Among the various dopants the Mo, Cr and W ions are considered as effective and influence the physical properties of the host glass owing to the fact that these ions may exist in different valence states with different environments simultaneously in the glass network.

To have a comprehensive understanding over the topology and valence states of molybdenum ions in PbO–Y$_2$O$_3$–P$_2$O$_5$ glass system, by a systematic
study of ESR spectra coupled with spectroscopic investigations (optical absorption, IR spectra). Hence the first part of thesis is devoted to these studies. Further, these glasses was simulated by their use in a variety of industrial applications, including sequestering agents for hard water treatments and dispersants for clay processing and pigment manufacturing. They are also the materials of choice particularly for high power laser applications. Such as infrared-absorbing glass, as well as camera and telescope lenses, because of the high refractive index and low dispersion of rare-earth glasses. The addition of Lanthanum (III) oxide (La$_2$O$_3$) improves the alkali resistance of glass, and is used in making special optical glasses. Hence the second part of thesis is devoted to these studies.

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. The aim of the present study is to explore the structural influence of WO$_3$ on PbO–Sc$_2$O$_3$–P$_2$O$_5$ glass system, by a systematic study of optical absorption, ESR and IR spectra. Hence the third part of thesis is devoted to these studies.

Thus the clear objectives of the present study are

- To have a comprehensive understanding over the influence of molybdenum ions on structural aspects of PbO–Y$_2$O$_3$–P$_2$O$_5$ glasses by investigating the optical absorption, ESR and IR spectra.
To have a broad perceptive over the role of chromium ions on the structure of PbO–La₂O₃–P₂O₅ glass system from a systematic study of spectroscopic studies.

To investigate the optical properties of WO₃ doped PbO–Sc₂O₃–P₂O₅ glasses

1.5 Contents of the present work

The glasses used for the present studies are:

1. 40 PbO– (10–x)Y₂O₃–P₂O₅: x MoO₃ (0 ≤ x ≤ 5)

2. 40 PbO– (10–x)La₂O₃–P₂O₅: x Cr₂O₃ (0 ≤ x ≤ 0.5)

3. 40 PbO– (10–x)Sc₂O₃–P₂O₅: x WO₃ (0 ≤ x ≤ 5)

The present study is devoted to have a comprehensive understanding over the influence of molybdenum, chromium and tungsten ions on the structural properties of this glass system by investigating a variety of physical properties. The thesis also contains the data on optical characterization of some transition metal oxide ions doped.

The studies carried out are:

(i) Differential Thermal Analysis and the evaluation of glass transition temperature Tᵣ.

(ii) Infrared spectral studies in the wavenumber range 400–2000 cm⁻¹ and the study of the effect of concentration of transition metal ions on the position and intensity of various vibrational bands.

(iii) Optical absorption studies in the wavelength range 300–1000 nm, identification of various electronic transitions of transition metal ions.
(iv) Electron spin resonance measurements at room temperature and the identification of the positions and valence states of transition metal ions in the glass network.
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