Magnetic and spectroscopic properties of PbO–La$_2$O$_3$–P$_2$O$_5$:Cr$_2$O$_3$ Glass System

PbO–La$_2$O$_3$–P$_2$O$_5$ glasses containing different concentrations of Cr$_2$O$_3$ ranging from 0 to 0.5 mol% were prepared. A number of studies viz., differential thermal analysis, infrared, optical absorption, ESR spectra and magnetic properties of these glasses has been carried out as a function of chromium ion concentration. The analysis of the results of these studies indicated that chromium ions mostly exist in Cr$^{3+}$ state in these glasses when the concentration of Cr$_2$O$_3$ ≤ 0.3mol% occupy octahedral positions and above this concentration chromium ions seem to subsist in Cr$^{6+}$ state and occupy tetrahedral positions with CrO$_2^-$ structural units.
Magnetic and spectroscopic properties of PbO–La$_2$O$_3$–P$_2$O$_5$: Cr$_2$O$_3$ glass system

4.1 Introduction

P$_2$O$_5$ glasses are well known due to their high thermal expansion coefficients (~20 to 27 X $10^{-6}$/°C) [1], low melting and softening temperatures and high ultra-violet and far infra red transmission [2, 3]. Interest on 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 [4]. They are also the materials of choice particularly for high power laser applications [5]. However, many phosphate glasses are volatile in nature, have poor chemical durability, highly hygroscopic in nature. These disadvantages have prevented the phosphate glasses from replacing the conventional glasses in a wide range of technological applications. In recent years there has been an enormous amount of research on improving the physical properties and the chemical durability of phosphate glasses by introducing a number of glass formers and modifiers such as Al$_2$O$_3$, MoO$_3$, Ga$_2$O$_3$, Cr$_2$O$_3$, Ta$_2$O$_5$, Sb$_2$O$_3$, As$_2$O$_3$ and etc., into P$_2$O$_5$ glass network [6, 7]. The addition of heavy metal oxides like PbO to the phosphate glasses is expected to improve the thermal stability of the glasses to a large extent. A considerable amount of work has been reported on PbO based glasses in the recent years [8, 9]. Earlier extensive investigations like Raman, FTIR, NMR, X-ray diffraction and various other studies [10, 11] on PbO–P$_2$O$_5$ glasses have revealed that, PbO takes the role of both glass former and glass
modifier. As 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. The addition of Lanthanum(III) oxide (La$_2$O$_3$) improves the alkali resistance of glass, and is used in making special optical glasses, 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.

Transition metal ions are being greatly used in the present days to probe the glass structure since their outer d-electron orbital function have a broad radial distribution and due to their high sensitive response to the changes in the surrounding actions. Among various transition metal ions, the chromium ion, a paramagnetic metal ion, when dissolved in glass matrices in very small quantities makes the glasses colored and has a strong influence over the optical properties of the glasses. It is due to the simple reason that it exists in different oxidation states viz., Cr$^{3+}$ (acting as modifier with CrO$_6$ structural units) and Cr$^{6+}$ (acting as network former with CrO$_4^{2-}$ structural units). The content of chromium in different states with different structural units in the glass depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strengths, mobility of the modifier cation, etc. Further, the most common optical absorption transition, $^4A_2 \rightarrow ^4T_2$ (which has a strong bearing on the luminescence efficiency) of Cr$^{3+}$ ion is found to be very sensitive to its chemical environment. Extensive investigations on the optical
absorption, luminescence and ESR spectroscopy of Cr$^{3+}$ ion in a variety of inorganic glasses have been made in recent years in view of their importance in the development of tunable solid state lasers and new luminescence materials [12–16].

Chromium ion a paramagnetic transitional metal ion, when dissolved in glass matrix even in very small quantities, makes the glasses coloured and has a strong influence over the physical properties of the glasses. These ions of various ionic radii can easily be incorporated in the glass host owing to a much looser and relaxed glass structure than that of crystalline media. Regardless of the oxidation state of the chromium in the starting glass batch, these ions may exist in different valence states simultaneously in the final glass and occupy a variety of sites with different crystal field strengths due to site variability and compositional disorder. Further, materials containing mixed valence chromium are of recent interest as cathode materials in rechargeable batteries owing to their very high energy density and high capacitance [17, 18]. Among various oxidation states of chromium ions, Cr$^{3+}$, Cr$^{4+}$, Cr$^{5+}$ and Cr$^{6+}$ are the most likely to be active and stable. Out of these, the Cr$^{6+}$ (d$^0$) ions have the closed shell configuration, participate in the glass network with CrO$_4^{2-}$ structural units and is expected to strengthen the host phosphate glass network. The Cr$^{5+}$ (d$^1$) ions either participate in the glass network with CrO$_4^{3-}$ complexes or go into the modifying positions with octahedral coordination. The Cr$^{3+}$ ions occupy octahedral sites and the efficiency of the most common lasing transition $^4T_2 \rightarrow ^4A_2$ of this ion is found to be very sensitive to the internal structure of the glass.
A large number of interesting studies are available on the coordination and oxidation states of chromium ion in various crystals, inorganic glass systems [19].

The Cr⁵⁺ (d¹) ions either participate in the glass network with CrO₄³⁻ complexes (in a tetrahedral field) or go into the modifying positions with octahedral coordination. For a d¹ transition metal ion like Cr⁵⁺, in an undistorted tetrahedral coordination, the ground state is ⁰E and the ligand field excited state is ⁰T₂. If CrO₄³⁻ tetrahedron is tetragonally elongated, the ⁰T₂ state splits into ²B₂ (dₓᵧ) and ²E (dₓz, dᵧz) components. As a result, two transitions are predicted [20] from the lower energy component of ⁰E to the two components of ⁰T₂. In fact, two bands in absorption spectra due to these two transitions of Cr⁵⁺ ions are reported in other glass systems [21, 22]. The energy level diagram for d¹ complexes in tetrahedral field is shown in Fig. 4.1(a).

![Energy level diagram for d¹ complexes in tetrahedral field](image)

**Fig. 4.1(a)** The splitting of d¹ energy levels in tetrahedral field

![Energy level diagram for d¹ complexes in an octahedral field](image)

**Fig. 4.1(b)** The splitting of d¹ energy levels in an octahedral field
The energy level diagram for $d^1$ ion complexes in an octahedral field is the inverse of that of the tetrahedral field as shown in Fig. 4.1(b). A detailed review on the chemistry of $\text{Cr}^{5+}$ ion is available in the literature [23, 24].

Similarly, the $\text{Cr}^{3+}$ ions occupy octahedral sites. A large number of interesting studies are available on the environment and oxidation states of chromium ion in various crystals, inorganic glass systems [25–27]. $\text{Cr}^{3+}$ ion has a $d^3$ electronic configuration. In the ground state these electrons occupy the $t_{2g}$ orbitals, i.e. $(t_{2g})^3$. The two $e_g$ orbitals are empty, providing two ‘holes’ into which the electrons can be promoted. The three unpaired electrons give rise to the free ion terms $^4F$, $^4P$, $^2G$ and several other doublet states of which $^4F$ is the ground state. In the octahedral field the $^4F$ state is split into $^4A_{2g}$ (F), $^4T_{2g}$ (F) and $^4T_{1g}$ (F) states, the $^4P$ state is not split but transforms into a $^4T_{1g}$ (P) state and the $^2G$ state splits into $^2A_{1g}$ (G), $^2T_{1g}$ (G), $^2T_{2g}$ (G) and $^2E_g$ (G). For convenience the free ion term and the corresponding crystal field terms are given in the parenthesis [28]. The states $^4A_{2g}$ (F), $^2E_g$ (G), $^2T_{1g}$ (G) and $^2T_{2g}$ (G) correspond to the lowest strong field configuration $(t_{2g})^3$. The states $^4T_{1g}$ (F) and $^4T_{2g}$ (F) correspond to $(t_{2g})^2(e_g)^1$ and $^4T_{1g}$ (P) corresponds to $(t_{2g}) (e_g)^2$. The ground state for $\text{Cr}^{3+}$ ions is $^4A_{2g}$ (F) at all strengths of the crystal field. $\text{Cr}^{3+}$ ions have the d-electron configuration and have larger octahedral site preference energy [28]. In an octahedral field, its ground level is $^4A_{2g}$. Under the field action of a low symmetry component and spin orbit coupling, the fourfold degenerate spin states split into two Kramers doublets.
The present investigation is intended to have a comprehensive understanding over the influence of chromium ions on the structure of PbO–La$_2$O$_3$–P$_2$O$_5$ glasses from a systematic study of the spectroscopic properties, viz., optical absorption, IR, ESR spectra and magnetic susceptibility along with differential thermal analysis.

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

- C$_0$: 40PbO–10 La$_2$O$_3$–50P$_2$O$_5$
- C$_1$: 40PbO–9.9 La$_2$O$_3$–50P$_2$O$_5$: 0.1 Cr$_2$O$_3$
- C$_2$: 40PbO–9.8 La$_2$O$_3$–50P$_2$O$_5$: 0.2 Cr$_2$O$_3$
- C$_3$: 40PbO–9.7 La$_2$O$_3$–50P$_2$O$_5$: 0.3 Cr$_2$O$_3$
- C$_4$: 40PbO–9.6 La$_2$O$_3$–50P$_2$O$_5$: 0.4 Cr$_2$O$_3$
- C$_5$: 40PbO–9.5 La$_2$O$_3$–50P$_2$O$_5$: 0.5 Cr$_2$O$_3$

### 4.2. Brief review of previous work on Cr$_2$O$_3$ doped glasses

S. Yusub et al [29] synthesized Li$_2$O–PbO–B$_2$O$_3$–P$_2$O$_5$ glasses containing different concentrations of Cr$_2$O$_3$ and studied dielectric properties, optical absorption and ESR spectra. M.A. Marzouk et al [30] investigated effects of gamma irradiation on spectral properties of Cr$_2$O$_3$-doped phosphate glasses of three varieties, namely sodium metaphosphate, lead metaphosphate and zinc metaphosphate. I.S. Yahia et al [31] have been prepared glass system with the composition xLa$_2$O$_3$–30PbO–(70–x)B$_2$O$_3$: (0 ≤ x ≤ 10 mol%) and studied the transmittance, reflectance spectra and the optical constants. R.S. Gedam et al
Salwa A.M. Abdel-Hameed et al [33] investigated effect of La$_2$O$_3$ addition on electrical and optical properties of 27.5Li$_2$O-(72.5–X) B$_2$O$_3$–XLa$_2$O$_3$. Prepared and characterized of ferromagnetic glass ceramic in the system Fe$_2$O$_3$–CaO–ZnO–SiO$_2$ with different nucleating agents. The effect of La$_2$O$_3$, CoO, Cr$_2$O$_3$ and MoO$_3$ as nucleating agents was investigated.

Hamdan. A. S. Al-Shamiri et al [34] prepared Sodium zinc Phosphate glasses containing different concentrations of chromium oxide and characterized by X-ray diffraction, FT-IR spectroscopy. Transmission, absorption and fluorescence as optical properties were also investigated. Bin Qian et al [35] studied structural properties of xLa$_2$O$_3$A(40–x)Fe$_2$O$_3$ A 60P$_2$O$_5$(x = 0,2,4,6,8,10 mol%) glasses and investigated by Fourier transform infrared spectrum (FTIR), X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Bozena Burtan et al [36] studied multicomponent telluride-tungstate glasses containing Nd$^{3+}$ and Er$^{3+}$ ions using spectroscopic methods. M. Abdelghany et al [37] investigated undoped and transition metals (3d TM) doped sodium borophosphate glasses. Experimental optical data indicate that the undoped sodium borophosphate glass reveals before irradiation strong and broad UV absorption and no visible bands identified. Kiran et al [38] have been studied electron paramagnetic resonance (EPR), optical absorption and emission spectra of Cr$^{3+}$ions doped in $(30-x)$ (NaPO$_3$)$_6$+30PbO+40B$_2$O$_3$+xCr$_2$O$_3$ $(x=0.5, 2.0, 3.0, 4.0$ and $5.0$ mol%) glasses. G.B. Devidas et al [39] have been investigated the glass transition temperature and electrical conductivity in the temperature range 325 K to 525 K in a set of
La$_2$O doped vanado-phosphate glasses. Srikumar et al [40] have been prepared Li$_2$O–ZrO$_2$–SiO$_2$: Ho$^{3+}$ glasses mixed with three interesting d-block elemental oxides, viz., Nb$_2$O$_5$, Ta$_2$O$_5$ and La$_2$O$_3$. Optical absorption and photoluminescence spectra of these glasses have been recorded at room temperature. The Judd–Ofelt theory was successfully applied to characterize Ho$^{3+}$ spectra of all the three glasses and conclude that among the three glasses studied the La$_2$O$_3$ mixed glass exhibited the highest quantum efficiency.

T. Srikumar et al [41] have been prepared Li$_2$O–ZrO$_2$–SiO$_2$: Nd$^{3+}$ glasses mixed with Nb$_2$O$_5$, Ta$_2$O$_5$ and La$_2$O$_3$ and studied optical absorption and photoluminescence spectra at room temperature. A. santic et al [42] studied influence of Cr$_2$O$_3$ on PbO–Fe$_2$O$_3$–P$_2$O$_5$ glasses and investigated by Raman and Mössbauer spectroscopies, X-ray diffraction analysis (XRD), Differential Thermal Analysis (DTA), Scanning Electron Microscopy (SEM) and impedance spectroscopy. Kesavulu et al [43] have reported the results on mixed alkali effect (MAE) in xLi$_2$O–(30–x)Cs$_2$O–69.25B$_2$O$_3$ ($5 \leq x \leq 2.5$) glasses doped with 0.75 mol% of Cr$^{3+}$ ions studied by electron paramagnetic resonance (EPR), optical absorption and luminescence techniques. Bala Murali Krishna et al [44] have studied the role of chromium ion valence states in ZnO-As$_2$O$_3$-Sb$_2$O$_3$ glass system by means of spectroscopic and dielectric studies. Sudhakar et al [45] have reported vibrational spectral analysis of structural modifications of Cr$_2$O$_3$ containing oxyfluoroborate glasses. The breaking and reforming of the boroxol ring is explained from the Raman spectral studies of these glasses. Pisarski et al [46] have reported transition metal (Cr$^{3+}$) and rare
earth (Eu$^{3+}$, Dy$^{3+}$) ions used as a spectroscopic probe in compositional-dependent lead borate glasses. They suggesting higher asymmetry and more covalent bonding character between rare earth and oxygen ions. Shao-Yi Wu et al. [47] have investigated the g factors and local structure for Cr$^{5+}$ within Cr$_2$O$_3$ nanocrystals embedded in the silica glass matrix by theoretical studies with the perturbation formulas and improved the previous treatments of EPR spectra and the assignments of the optical transitions based on approximate tetragonal (D$_{2d}$) symmetry by inducing slight orthorhombic distortion in their work. By means of spectroscopic and dielectric relaxation studies. Singh et al. [48] reported that M$_2$O$_3$ plays an important role in controlling the chemical durability and bioactivity of the glasses.

G. Murali Krishna et al. [49] prepared Li$_2$O–CaF$_2$–P$_2$O$_5$ glasses mixed with different concentrations of Cr$_2$O$_3$ and characterized by X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy (EDS), differential thermal analysis and conventional spectroscopic techniques. Ashutosh Goel et al. [50] have been reported on the effect of La$_2$O$_3$ and Cr$_2$O$_3$ on the structural, thermal and crystallization behavior of diopside-based glasses and on the processing, microstructure and properties of the sintered glass-ceramics. Veerabhadra Rao et al. [51] investigated the dielectric dispersion in PbO–PbF$_2$–B$_2$O$_3$ glass system doped with Cr$_2$O$_3$. The results have been analysed in the light of different oxidation states of chromium ions with aid of the data on differential scanning calorimetry, infrared, optical absorption and ESR spectra. Srinivasa Reddy et al. [52] reported the valence and coordination
of chromium ions in ZnO–Sb₂O₃–B₂O₃ glass system. By the analysis of thermo-optical properties of lithium aluminum silicate glasses doped with Cr³⁺ ions.

Marcio Luís Ferreira Nascimento et al [53] Differential scanning calorimetry (DSC) was used to study the effect of La₂O₃ addition on crystallization mechanism of barium–lead–zinc phosphate glasses. A. Santic et al [54] The structural properties of xCr₂O₃–(40–x)Fe₂O₃–60P₂O₅, 0 ≤ x ≤ 10 (mol%) glasses have been investigated by Raman and Mössbauer spectroscopy, X-ray diffraction (XRD) and differential scanning calorimetry (DSC). G. Little Flower et al [55] have been studied influence of Chromium Ions on the Dielectric Properties of the PbO–Ga₂O₃–P₂O₅ Glass System. The dielectric properties have been studied as a function of the concentration of chromium ions. Little Flower et al [56] prepared PbO–Ga₂O₃–P₂O₅ glasses containing different concentrations of Cr₂O₃ and studied a number of studies viz., differential thermal analysis, infrared, optical absorption, ESR and Raman spectra as a function of chromium ion concentration.

Fouad El-Diasty et al [57] have been reported review of the fundamentals and recent research advances in optical properties of oxide glasses containing chromium reported by Manal Abdel-Baki and Fouad El-Diasty [58]. With the bonding parameters obtained from optical and EPR investigations. Naga Raju et al [59] have investigated the structural role of chromium ions on the improvement of insulating character of ZnO–ZnF₂–B₂O₃ glass system by means of dielectric, spectroscopic and magnetic properties. Laxmi Kanth et al [60] have studied spectroscopic investigations on ZnF₂–
MO–TeO$_2$ (MO=ZnO, CdO and PbO) glasses doped with chromium ions. Ravikumar et al [61] reported covalent nature for Cr$^{3+}$ ion in chromium doped zinc phosphate glasses. Sreekanth Chakradhar et al [62] reported the optical absorption and EPR structural studies of chromium ions in alkali lead borotellurite glasses. Rodriguez-Mendoza et al [63] have interpreted the absorption and emission spectra of the Cr$^{3+}$ ions in tantalum tellurite glasses considering the Cr$^{3+}$ ions in an actahedral (Oh) environment. Ardelean and Filip et al [64] have studied electron paramagnetic resonance and magnetic susceptibility measurements on TeO$_2$ based glasses containing transition metal ions (Cr$^{3+}$, Fe$^{3+}$, Mn$^{2+}$ and Cu$^{2+}$). Raghavaiah and Veeraiah et al [65] investigated the dielectric and spectroscopic properties of 40 PbO-(60-x)Sb$_2$O$_3$-x As$_2$O$_3$:0.4Cr$_2$O$_3$ (with x ranging from 10 to 55 mol%) and reported that lower concentrations of As$_2$O$_3$ glasses exhibits more favourable environment for the presence of larger concentrations of laser-emitting Cr$^{3+}$ ions in the composition. Koepke et al [66] have investigated the presence of various states of chromium ions (Cr$^{3+}$, Cr$^{4+}$, Cr$^{5+}$, Cr$^{6+}$) in the ZrO$_2$-Al$_2$O$_3$-SiO$_2$, Li$_2$B$_4$O$_7$ glasses and in the silica sol-gel glass, and reported that the first two glass systems are hosting the Cr$^{3+}$ ions, while the sol-gel silica glass doesn.t.

Venkateswara Rao and Veeraiah et al [67] reported study on certain physical properties of R$_2$O-CaF$_2$-B$_2$O$_3$: Cr$_2$O$_3$ glasses and the analysis indicate the presence of a part of the chromium ions in the Cr$^{6+}$ state adopting network forming positions. D.K.Durga et al [68] Clear glasses of the system, ZnF$_2$–As$_2$O$_3$–TeO$_2$, containing different concentrations of Cr$_2$O$_3$ (ranging from 0 to
0.6 wt%) were prepared. A number of studies viz., differential thermal analysis, infrared spectra, optical absorption, ESR, magnetic susceptibility, thermoluminescence and dielectric properties, on these glasses were carried out as a function of chromium ion concentration. D.K. Durga et al [69] Optical absorption, thermoluminescence, infrared spectra and differential thermal analysis of three different tellurite glass systems viz., ZnF$_2$–As$_2$O$_3$–TeO$_2$, ZnF$_2$–Bi$_2$O$_3$–TeO$_2$ and ZnF$_2$–P$_2$O$_5$–TeO$_2$ containing 0.4% of Cr$_2$O$_3$, have been investigated. Strek et al [70] have performed the EPR and optical measurements on Cr-doped silica sol-gel glasses and concluded that the EPR signal is associated with Cr$^{5+}$ ions at tetrahedral sites whereas the emission is attributed to ligand-metal charge transfer transitions of Cr$^{6+}$ ions coupled to Cr$^{5+}$ and absence of Cr$^{3+}$ ions in silica gel glasses. Ardelean et al [71] investigated EPR and magnetic susceptibility studies of Cr$_2$O$_3$–Bi$_2$O$_3$–GeO$_2$ glasses. In the composition of 40SiO$_2$–30BaO–20B$_2$O$_3$–30CaO–10M$_2$O$_3$ (M=Al, Cr, Y and La) glasses. Wanda Jungowska Strek et al [72] The system La(PO$_3$)$_3$–Ca(PO$_3$)$_2$–P$_2$O$_5$ was investigated using the methods of thermal analysis and X-ray powder diffraction, and its phase diagram was obtained. The occurrence of a ternary compound CaLa(PO$_3$)$_5$, which was peritectically formed at a temperature of 900°C and, with respect to its stoichiometry, was situated in the system La(PO$_3$)$_3$–Ca(PO$_3$)$_2$, was found. The phosphate CaLa(PO$_3$)$_5$ with lanthanum ultra phosphate gives the pseudobinary system CaLa(PO$_3$)$_5$–LaP$_5$O$_{14}$. The related phase diagram, as well as a one for the side system La(PO$_3$)$_3$–Ca(PO$_3$)$_2$, was obtained.
4.3 Characterization

4.3.1 XRD

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

4.3.2 Physical Parameters

The physical parameters such as molybdenum ion concentration $N_i$ and mean chromium ion separation $r_i$, molar volume ($V_M$) of these glasses are evaluated from the measured values of density $d$ and calculated average molecular weight $\bar{M}$, using the conventional formulae and are presented in Table 4.1.

**Table 4.1**

<table>
<thead>
<tr>
<th>Glass</th>
<th>Density $d$ (g/cm$^3$) $\pm 0.001$</th>
<th>Average molecular weight, $\bar{M}$ (g/mol) $\pm 0.001$</th>
<th>Conc. of Chromium ions, $N_i$ (10$^{22}$/cm$^3$) $\pm 0.00001$</th>
<th>Interionic distance $R_i$ (Å) $\pm 0.0001$</th>
<th>Polaron radius $R_p$ (Å) $\pm 0.0001$</th>
<th>Field Strength $F_i$ (10$^{16}$, cm$^{-2}$) $\pm 0.000001$</th>
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<tr>
<td>$C_0$</td>
<td>5.658</td>
<td>192.831</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>$C_1$</td>
<td>5.663</td>
<td>192.982</td>
<td>1.767</td>
<td>8.27081</td>
<td>3.3326</td>
<td>0.54025</td>
</tr>
<tr>
<td>$C_2$</td>
<td>5.668</td>
<td>193.134</td>
<td>3.535</td>
<td>6.56425</td>
<td>2.6449</td>
<td>0.85767</td>
</tr>
<tr>
<td>$C_3$</td>
<td>5.673</td>
<td>193.286</td>
<td>5.303</td>
<td>5.73414</td>
<td>2.3105</td>
<td>1.12397</td>
</tr>
<tr>
<td>$C_4$</td>
<td>5.678</td>
<td>193.438</td>
<td>7.072</td>
<td>5.20958</td>
<td>2.0991</td>
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<tr>
<td>$C_5$</td>
<td>5.684</td>
<td>193.591</td>
<td>8.842</td>
<td>4.83593</td>
<td>1.9485</td>
<td>1.58027</td>
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</table>
4.3.3 Differential thermal analysis (DTA) studies

In the Fig. 4.2 scans for PbO–La$_2$O$_3$–P$_2$O$_5$ glasses doped with different concentrations Cr$_2$O$_3$ 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 325 and 350$^\circ$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 4.2. Among all the glasses, the glass C$_5$ (glass containing 0.5 mol% of Cr$_2$O$_3$), exhibited the highest value of $(T_c-T_g)$.

<table>
<thead>
<tr>
<th>Glass</th>
<th>$T_g$ ($^\circ$C)</th>
<th>$T_c$ ($^\circ$C)</th>
<th>$T_c$–$T_g$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_0$</td>
<td>325 ($\pm 1^\circ$C)</td>
<td>756 ($\pm 1^\circ$C)</td>
<td>431 ($\pm 1^\circ$C)</td>
</tr>
<tr>
<td>$C_1$</td>
<td>291 ($\pm 1^\circ$C)</td>
<td>720 ($\pm 1^\circ$C)</td>
<td>429 ($\pm 1^\circ$C)</td>
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<td>$C_2$</td>
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<td>427 ($\pm 1^\circ$C)</td>
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<tr>
<td>$C_3$</td>
<td>330 ($\pm 1^\circ$C)</td>
<td>785 ($\pm 1^\circ$C)</td>
<td>455 ($\pm 1^\circ$C)</td>
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<tr>
<td>$C_4$</td>
<td>335 ($\pm 1^\circ$C)</td>
<td>792 ($\pm 1^\circ$C)</td>
<td>457 ($\pm 1^\circ$C)</td>
</tr>
<tr>
<td>$C_5$</td>
<td>350 ($\pm 1^\circ$C)</td>
<td>815 ($\pm 1^\circ$C)</td>
<td>465 ($\pm 1^\circ$C)</td>
</tr>
</tbody>
</table>
4.4 Results

4.4.1 Optical absorption

Fig. 4.3(a) presents optical absorption spectra of PbO–La₂O₃–P₂O₅ glasses samples recorded at room temperature in the wavelength region 300–1000 nm. containing different concentrations of Cr₂O₃. The spectrum of glass C₁, has exhibited two prominent absorption bands with the peaks at 433 nm (peak 1) and 662 nm (peak 2); with increasing concentration of Cr₂O₃ 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 C₄ and C₅. Two additional shoulders at 670 and 700 nm have also been observed on peak-2 of all the glasses. From the spectra we observe that the cutoff wavelength shifted towards higher wavelength with increase in the concentration of Cr₂O₃ up to 0.3 mol% and there after the edge is shifted gradually towards lower wavelength. The cut off wavelengths, band positions and optical band gaps of the present glass systems are shown in Table 4.3.

From the observed absorption edges, we have evaluated the optical band gaps (E₀) of these glasses by drawing a plot between \((\alpha \hbar \omega)^{1/2}\) and \(\hbar \omega\) as per the equation

\[
\alpha (\omega) \hbar \omega = C (\hbar \omega - E_0)^2
\]

Fig. 4.3(b) represents such plots of all these glasses a considerable part of each curve is observed to be linear. The values of optical band gap (E₀) obtained from the extrapolation of linear portions in the plots are furnished in Table 4.3, the value of E₀ is found to be the highest (3.40 eV) for glass C₅ and the lowest (3.18 eV) for glass C₃.
Table 4.3

Data on optical absorption spectra of PbO–La$_2$O$_3$–P$_2$O$_5$–Cr$_2$O$_3$ glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>Cutoff wavelength (nm)</th>
<th>Optical band gap (eV)</th>
<th>Band positions (nm)</th>
<th>$D_q$ (cm$^{-1}$)</th>
<th>B (cm$^{-1}$)</th>
<th>Nephelauxetic ratio, $\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_0$</td>
<td>381</td>
<td>3.16</td>
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<tr>
<td>C$_1$</td>
<td>362</td>
<td>3.34</td>
<td>433.0</td>
<td>662.0</td>
<td>1524.0</td>
<td>746.0</td>
</tr>
<tr>
<td>C$_2$</td>
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<td>3.32</td>
<td>434.5</td>
<td>664.0</td>
<td>1523.2</td>
<td>746.5</td>
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<td>435.0</td>
<td>665.0</td>
<td>1522.3</td>
<td>747.0</td>
</tr>
<tr>
<td>C$_4$</td>
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<td>3.38</td>
<td>435.5</td>
<td>652.0</td>
<td>1524.5</td>
<td>732.1</td>
</tr>
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<td>C$_5$</td>
<td>356</td>
<td>3.40</td>
<td>437.0</td>
<td>650.0</td>
<td>1528.0</td>
<td>712.0</td>
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</table>
Fig. 4.3(a) Optical absorption spectra of PbO–La₂O₃–P₂O₅–Cr₂O₃ glasses. All the transitions are from ground state $^4A_2$. 
Fig. 4.3(b) Urbach plots for PbO-La$_2$O$_3$-P$_2$O$_5$. Cr$_2$O$_3$ glasses.
4.4.2 ESR spectra

ESR spectra of PbO–La$_2$O$_3$–P$_2$O$_5$ glasses doped with different concentrations of Cr$_2$O$_3$ recorded at room temperature are shown in Fig. 4.4. 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%. From the values of susceptibility, the concentration of the Cr$^{3+}$ions ($N'$) that contribute to the paramagnetic susceptibility is evaluated (by taking the value of effective magnetic moment, $\mu_{\text{eff}} = 3.8\mu_\text{B}$) and presented in Table 4.4.
Table 4.4
Data on magnetic susceptibility and other related parameters of PbO–La$_2$O$_3$–P$_2$O$_5$:Cr$_2$O$_3$ glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Total chromium ions conc. $N_i$ ($10^{22}$ ions/cm$^3$)</th>
<th>$\chi$ ($10^{-5}$, emu)</th>
<th>Cr$^{3+}$ ion conc. $N'$ ($10^{22}$ ions/cm$^3$)</th>
<th>$N'/N_i$</th>
<th>g</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$</td>
<td>1.767</td>
<td>0.540</td>
<td>1.705</td>
<td>0.965</td>
<td>1.983</td>
<td>0.385</td>
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<td>$C_2$</td>
<td>3.535</td>
<td>0.783</td>
<td>3.429</td>
<td>0.970</td>
<td>1.983</td>
<td>0.385</td>
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<td>$C_3$</td>
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<td>1.062</td>
<td>5.224</td>
<td>0.985</td>
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<td>0.385</td>
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<tr>
<td>$C_4$</td>
<td>7.072</td>
<td>1.584</td>
<td>6.379</td>
<td>0.902</td>
<td>1.987</td>
<td>0.316</td>
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<tr>
<td>$C_5$</td>
<td>8.842</td>
<td>1.943</td>
<td>7.913</td>
<td>0.895</td>
<td>1.991</td>
<td>0.221</td>
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</table>
4.4.3 IR spectra

The infrared transmission spectra of PbO–La$_2$O$_3$–P$_2$O$_5$ glasses doped with different concentration of Cr$_2$O$_3$ (Fig. 4.5) exhibit vibrational bands at about 1250 cm$^{-1}$ (identified due to P=O stretching vibration, this region may also consist of bands due to anti-symmetrical vibrations of PO$_2^-$ groups), 1050 cm$^{-1}$ (a normal vibrational mode in PO$_3^{3-4}$ 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 [73, 74]. A band due to PbO$_4$ structural units with the growing intensity with the concentration of
Cr$_2$O$_3$ (especially beyond 0.3 mol %) is also observed in the spectra of all these glasses at about 470 cm$^{-1}$ [75]. With the introduction of Cr$_2$O$_3$ (up to 0.3 mol%), the intensity of bands due to P=O, PO$_{3-4}$ and P–O–P are observed to decrease, for further increase of Cr$_2$O$_3$ content, the intensity of these bands is observed to increase (Fig. 4.5). It may be noted here that the band positions of various phosphate structural groups observed for the present samples are found to be well within the ranges reported in the literature [73, 74]. Additionally, in the spectra of glasses especially C$_3$ to C$_5$, a band at about 890 cm$^{-1}$ due to $\gamma_3$ vibrations of CrO$_{2-4}$ structural units (the intensity of which is increasing with the concentration of Cr$_2$O$_3$) is also observed [75].
Fig. 4.5. IR spectra of PbO–La₂O₃–P₂O₅–Cr₂O₃ glasses.
4.5 Discussion

PbO in addition to participating in the glass network with PbO$_4$ structural units (evidenced from IR spectra) it may also enter as modifier by transforming two Q$^3$-tetrahedra (viz., PO$_4$ tetrahedra with three bridging oxygens and one terminal de-bonded oxygen) into two Q$^2$-tetrahedra (viz., PO$_4$ tetrahedra with two bridging oxygens and two terminal de-bonded oxygen). And thus a PbO polyhedron is formed when it is surrounded by such two Q$^2$ and several Q$^3$ tetrahedrons. The previous studies show that there is no significant difference between the lanthanum-free glass and the glasses containing La$_2$O$_3$. The structure of the phosphate chains is not evidently affected by La$^{3+}$ in the glasses [76].

With the introduction of chromium ions up to 0.3 mol%, the value of the glass transition temperature $T_g$ and parameter $(T_c-T_g)$, have been observed to decrease and above 0.3 mol% the value of $T_g$ and $(T_c-T_g)$ is observed to increase. The augmented cross-link density and closeness of packing are responsible for such an increase of these parameters. This result clearly suggests that above 0.3mol%, chromium ions mostly occupy network forming positions with CrO$_2$ tetrahedral units and increase the cross-link density and strengthen the mean bond strength and increase the rigidity of the PbO–La$_2$O$_3$–P$_2$O$_5$ glass network.

With the introduction of chromium ions ($\leq$ 0.3 mol %), two intense absorption bands at 433 and 662 nm are observed in the optical absorption spectra. These two bands have been identified due to transitions of Cr$^{3+}$ (d$^3$)
ions; using Tanabe–Sugano diagrams for $d^3$ ion, the spectra have been analyzed and the bands are assigned to $^4A_2 \rightarrow ^4T_1(F), ^4A_2 \rightarrow ^4T_2$ transitions respectively. The corresponding LF parameters $D_q$ (crystal field splitting energy) and $B$ (Racah parameter, measure of the Coulomb repulsion among the 3d electrons of Cr$^{3+}$ion) have been evaluated and presented in Table 4.3. Using these values, the nephelauxetic ratio, i.e, $\beta = B_{\text{complex}}/B_{\text{free ion}}$ has also been evaluated for all the glasses and presented in Table 4.3, the value of $\beta$ is observed to be the highest for glass C$_3$ and the lowest for glass C$_5$. 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 $^4A_2 \rightarrow ^2T_1$ and $^4A_2 \rightarrow ^2E$ (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 [77]. Further, a decrease in the widths of $^2E$ and $^2T_1$ bands has clearly been observed with increase in the concentration of chromium ions form 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 [78]. Yet, this result can be interpreted in a different way as follows: as the concentration of Cr$^{3+}$ ions decreases in the glass network, there is a possibility for the decoupling of Cr$^{3+}$ ions with the Cr$^{6+}$ ions. Such decoupling makes the
transitions spin disallowed and responsible for decrease in the intensity of these two bands [79].

As the concentration of Cr$_2$O$_3$ raised beyond 0.3 mol% a new band predicted due to Cr (VI) ions is observed at 370 nm [80]. The Cr (VI) ions exist in the form of Cr$^{6+}$O$^{2-}$ centers in the frame of CrO$_2$ groups [81]. Cr$^{6+}$ ion belongs to d$^0$ closed shell and does not have electrons in d shell. Hence, this band is the transformation of chromium ions from Cr$^{6+}$ (3d$^0$2p$^6$) state into Cr$^{5+}$ (3d$^1$2p$^5$) state (charge transfer) or we may consider it as due to the excitation of p electron (involved in the ligand bonds of the t1π symmetry) into the d shell. The energy level of Cr$^{5+}$ ion with 3d$^1$2p$^5$ electronic configuration splits into two states of symmetry viz., 2e and 4t$_2$. In view of this, we may expect two charge transfer bands corresponding to the following transitions from Cr$^{6+}$ ions [82, 83]. Cr$^{6+}$ (3d$^0$2p$^6$) → Cr$^{5+}$ (3d$^1$2p$^5$) (t$_5^1$, 2e) and Cr$^{6+}$ (3d$^0$2p$^6$) → Cr$^{5+}$ (3d$^1$2p$^5$) (t$_5^1$, 4t$_2$). Among these two, the band observed at about 370 nm can be ascribed to the first transition where as the band due to second transition (high energy transition) band lies well below the cut-off wavelength as mentioned above. Thus the analysis of the results of the optical absorption spectra indicates (with the increase in the content of chromium ions in the glass network beyond 0.3 mol%), a gradual decrease in the concentration of octahedrally positioned Cr$^{3+}$ ions accompanied by a simultaneous increase in concentration of Cr$^{6+}$ ions, that take part network forming positions with CrO$_2$ structural units. Unlike Cr$^{3+}$ modifier ions, these Cr$^{6+}$ ions decrease the degree of depolymerisation of the glass network and reduce the bonding defects and
non-bridging oxygens (NBOs). The higher the concentration of such network formers, the lower is the concentration of NBOs in the glass matrix. This leads to a decrease in the degree of localization of electrons thereby decreasing the donor centers in the glass matrix. The decreasing presence of these donor centers increases the optical band gap and shifts the absorption edge towards lower wavelength side as observed when the concentration Cr$_2$O$_3$ is increased from 0.3 to 0.5 mol% [84]. With increase in the concentration of Cr$_2$O$_3$ up to 0.3 mol% the intensity of the bands due to P=O, PO$_3^{-4}$ and P–O–P symmetric bending vibrations is observed to decrease. Whereas the intensity of the band due to PO$_4$ bending torsional vibrational band is observed to increase. These results suggest that in this concentration range chromium ions mostly exist in tri-valence state, act as modifiers and disturb the glass network. However, when the concentration Cr$_2$O$_3$ is raised beyond 0.3 mol%, the chromium ions seem to exist in Cr$^{6+}$ state (evidenced from optical absorption spectra), participate in the glass network forming with CrO$_2^{-4}$ structural units, alternate with PO$_4$ units, such linkages may be responsible for the observed increase in the intensity of the symmetrical bands mentioned above in IR spectra.

The magnetic properties of these glasses arise from 3d$^3$ electrons of paramagnetic Cr$^{3+}$ ions. The fraction ($N'/N_i$), i.e., the ratio of Cr$^{3+}$ ions ($N'$) that contribute to the paramagnetic susceptibility to the total chromium ion concentration ($N_i$) is found to be the highest for glass C$_3$ and is observed to decrease gradually beyond this concentration (Table 4.4), thus supporting the view point, i.e., an increasing presence of Cr$^{6+}$ ions in the glasses C$_4$ and C$_5$. 
As mentioned in the optical absorption, in an octahedral field, the ground level of the Cr\(^{3+}\)(d\(^3\)) ion is \(^4\)A\(_{2g}\); under the action of a low symmetry field component and spin–orbit coupling, the four-fold degenerate spin-state splits into two Kramers doublets with the resonance signals of g~2 and 5 as observed. According to the theory of Landry the low field line with g~5 is attributed to the isolated Cr\(^{3+}\) ions that have local rhombic symmetry [85–87]. The absorption signal at g~2, may be the resultant of contributions, from both Cr\(^{3+}\) and Cr\(^{5+}\) ions [85, 88–90]. In earlier investigations on a number of other glass systems containing chromium ions, two closely separated absorption lines, one due to Cr\(^{3+}\) ions and the other due to Cr\(^{5+}\) or CrO\(^3\)\(_{-4}\) ions at a field around g = 2 have been reported [85,91, 92]. The molecular orbital level schemes proposed by Ballhausen and Liehr [93] predict that the unpaired electron in the unperturbed tetrahedral CrO\(^3\)\(_{-4}\) is in a double degenerate \(^2\)E level. The relaxation for the non-magnetic doublet is expected to be fast enough to make the ESR unobservable at the room temperature [92]. Probably, this is the reason, why the resolution of the two absorption lines could not be observed in the spectra of the present glasses. The kink observed at g = 4.2 may be due to the inadvertent presence of the traces of Fe\(^{3+}\) ion impurity [94, 95]. Comparatively larger intensity of low field peak (g~5) for glass C\(_3\) indicates higher concentrations of octahedrally positioned Cr\(^{3+}\) ions in this glass network. 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 [85] and (ii) due to the presence of large concentration of chromium ions in Cr$^{6+}$ state. Out of these, the first possibility seems to be unreasonable in this case, since the DTA studies predict high glass-forming ability for the glasses containing Cr$_2$O$_3$ beyond 0.3 mol%. The value of $\alpha$, the orbital reduction factor that gives information on the ionic contribution of the chemical bond, is evaluated by the equation [96].

$$g_0 = g_e - \frac{6\pi\lambda}{\Delta} \quad (4.2)$$

here $g_0$ is the $g$-value obtained in the present measurements, $g_e$ is the free electron $g$-factor equal to 2.0023, $\lambda$ is the spin–orbit coupling constant and $\Delta$ is the energy gap between $^4A_{2g}(F) \rightarrow ^4T_{2g}(F)$. The value of $\alpha$ obtained for all the glasses is furnished in Table 4.4. The smaller the value of $\alpha$, the larger is the covalent contribution to the chemical bond [96]. For the present glasses we have observed the value of $\alpha$ to decrease from glass C$_3$ to glass C$_5$. Thus, the measurements on ESR spectra of the present glasses also predict more ionic environment of chromium ions in the network of glass C$_3$ and more covalent environment in the network of glass C$_5$.

4.6 Conclusions

PbO–La$_2$O$_3$–P$_2$O$_5$ glasses mixed with different concentrations of Cr$_2$O$_3$ (ranging from 0 to 0.5 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 DTA studies predict an increasing glass forming ability of the glasses when the concentration of Cr$_2$O$_3$ is greater than 0.3 mol%.

2. Spectroscopic and magnetic studies indicate that there is an increasing presence of Cr$^{6+}$ ions in the glass network that take part network forming positions with CrO$_2^{-4}$ structural units and decrease the degree of disorder in the glass, when Cr$_2$O$_3$ is present in higher concentrations (>0.3 mol%). Hence these glasses are more useful for practical applications than pure PbO–P$_2$O$_5$ glasses.
References


