The role of chromium ions on dielectric and spectroscopic properties of Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$ glasses

4.1 Introduction

Nowadays much attention is paid towards borophosphate glasses due to their low refractive index, menial dispersion, remarkable optical properties and high transparency from the ultraviolet to the near-infrared region [1,2]. The chemical durability of borophosphate glasses doped with transition metals is greater than that of phosphate glasses due to the composition boron oxide in the glass network, mostly in the form of BO$_4$ tetrahedral, which transforms metaphosphate chain into three-dimensional network [3]. Due to these special properties, these glasses are used as materials for optical components such as tunable solid state lasers, optical materials, optical filters, IR domes, memories, modulators, luminescence materials, phosphors, solar energy converters, fiber optic communication devices, radiation dosimetry, cathode materials in batteries and in a number of electronic gadgets [4-10]. The conductivity of borate glasses integrated with multivalent transition metal ions can be enhanced by adding Li$_2$O to the glass network. The mixed electronic and ionic conduction of these glasses depend on the glass composition.

Among all the transition metal ions, chromium ions have attracted the attention of researchers due to their extraordinary absorption and emission properties when they occupy the octahedral positions in the host glass [11]. Chromium, a quite economical ion when dissolved in the glass network even in a
very small concentration makes the glass colored and influences the optical and
dielectric properties very strongly [12]. Cr$^{3+}$ ion is used to explore the structure
and local symmetry of new glass materials. In glass phases these ions occupy
different sites with different field strengths due to changes in position and
compositional disorder. Glasses combined with mixed valence chromium ions are
used as cathode materials in rechargeable batteries because of their high energy
density and lofty capacitance [12,13]. Chromium ions are expected to increase or
decrease the chemical durability, mechanical strength and conductivity of the
glasses hence they occupy in different oxidation states. These ions exist in glasses
in Cr$^{3+}$ states with CrO$_6$ structural units (acting as modifiers), Cr$^{5+}$ and Cr$^{6+}$ states
with CrO$_4^{3-}$ and CrO$_4^{2-}$ structural units respectively (playing the role of glass
formers) basing on the quantitative properties of glass formers, modifiers, size of
the ions in the glass network, their field strength and mobility of the modifying
cation [14-16].

Literature survey on borophosphate glasses reveals that most of the studies
on these glasses are confined to structural investigation by means of DSC and
spectroscopic studies etc. Particularly, no considerable studies on dielectric
properties (dielectric constant $\varepsilon'$, loss factor tan$\delta$, a.c. conductivity $\sigma_{ac}$ and
dielectric breakdown strength) of chromium doped lithium lead borophosphate
glasses are available. These studies are vital in estimating the conductivity and
topology of the glasses. The main objective of the present investigation is to make
a comprehensive study on the influence of chromium ions on the structural aspects
of lithium lead borophosphate glasses from a systematic study on dielectric properties and spectroscopic studies such as optical absorption, FTIR and ESR spectra.

Hence this chapter is aimed at an overall understanding of valence states and the local environment of chromium ions (introduced as Cr\(_2\)O\(_3\)) in Li\(_2\)O-PbO-B\(_2\)O\(_3\)-P\(_2\)O\(_5\) glass network and to explore the role of chromium ions on the structural modifications that take place in the glass network by means of spectroscopic viz., optical absorption, FTIR, ESR and dielectric studies.

For the present investigation particular composition is chosen: 10Li\(_2\)O-20PbO-45B\(_2\)O\(_3\)-(15-x)P\(_2\)O\(_5\): xCr\(_2\)O\(_3\) (all in mol %) with 0 ≤ x ≤ 1. The details are:

C0: 10Li\(_2\)O-20PbO-45B\(_2\)O\(_3\)-15P\(_2\)O\(_5\)
C1: 10Li\(_2\)O-20PbO-45B\(_2\)O\(_3\)-14.9P\(_2\)O\(_5\): 0.1Cr\(_2\)O\(_3\)
C2: 10Li\(_2\)O-20PbO-45B\(_2\)O\(_3\)-14.7P\(_2\)O\(_5\): 0.3Cr\(_2\)O\(_3\)
C3: 10Li\(_2\)O-20PbO-45B\(_2\)O\(_3\)-14.5P\(_2\)O\(_5\): 0.5Cr\(_2\)O\(_3\)
C4: 10Li\(_2\)O-20PbO-45B\(_2\)O\(_3\)-14.2P\(_2\)O\(_5\): 0.8Cr\(_2\)O\(_3\)
C5: 10Li\(_2\)O-20PbO-45B\(_2\)O\(_3\)-14.0P\(_2\)O\(_5\): 1.0Cr\(_2\)O\(_3\) (all in mol%)

4.2 Brief review of the previous work on chromium ions doped glasses

V.K. Deshpande and Thomas Philip [17] have investigated the effect of Cr\(_2\)O\(_3\) addition on the variation in electrical conductivity, density and T\(_g\) in Li\(_2\)O-B\(_2\)O\(_3\)-SiO\(_2\) glass network. The results have been analyzed in the light of the NBOs present in the glass, the electronic contribution to the total conductivity, the size and mass of the Cr\(^{3+}\) ion which is substituted for B\(_2\)O\(_3\) and SiO\(_2\) in the glass. Apart
from dielectric and spectroscopic studies, thermo luminescence studies were carried out on 19PbO-5Al2O3-(76-x)B2O3: xCr2O3 with 0 ≤ x ≤ 0.4 in steps of 0.1 (all in mol%) by Rami Reddy et al. [18] where in it is reported that at the lowest concentration only the Cr³⁺ ions dominate in the glass network adopting network modifying positions. Gan Fuxi et al. [19] have studied the ESR spectra of Cr³⁺ ions in phosphate, fluorophosphates and fluoride glasses; they have calculated the energy level splitting and the effective g value of the Cr³⁺ ion with the spin Hamiltonian. By means of spectroscopic and dielectric relaxation studies Srinivasa Reddy et al. [20] reported the valence and coordination of chromium ions in ZnO–Sb₂O₃–B₂O₃ glass system. Sreekanth Chakradhar et al. [21] reported the optical absorption and EPR structural studies of chromium ions in alkali lead borotellurite glasses. Ardelean and Filip [22] have performed electron paramagnetic resonance and magnetic susceptibility measurements on TeO₂ based glasses containing transition metal ions (Cr³⁺, Fe³⁺, Mn²⁺ and Cu²⁺) and concluded that the local environment, structural distributions, valence states and strength of magnetic interactions depend of the nature and concentration of transition metal ions.

Koepke et al. [23] have examined the presence of various states of chromium ions (Cr³⁺, Cr⁴⁺, Cr⁵⁺, Cr⁶⁺) in the ZrO₂–Al₂O₃–SiO₂, Li₂B₄O₇ glasses and in the silica sol–gel glass, and explored that the first two glass systems are hosting the Cr³⁺ ions, while the sol-gel silica glass doesn’t. Investigating the change of the Cr³⁺ environment during the xerogel-glass-glass ceramic transformation in the SiO₂–Al₂O₃–ZnO–Cr₂O₃ and SiO₂–Al₂O₃–MgO–Cr₂O₃...
systems, by means of absorption and emission spectra, electron paramagnetic resonance measurements and site-selective laser spectroscopy, Costa et al. [24] interpreted the structural considerations exhibiting the variation of Cr\(^{3+}\) environment during heat treatment. Dance et al. [25] have performed EPR experiments on fluoroaluminate glasses doped with chromium ions and concluded that these ions occupy sites of fully rhombic symmetry. Lakshmana Rao et al. [26] have reported the changes in ESR and optical absorption spectra of Cr\(^{3+}\) ions in \(\text{K}_2\text{SO}_4-\text{ZnSO}_4\) glasses with the temperature and the concentration of chromium ions. They have attributed the low field spectral line observed in ESR spectrum to isolated Cr\(^{3+}\) ions whereas the high field spectral line to exchange coupled pairs of Cr\(^{3+}\) ions.

By means of X-Ray diffraction, FTIR and optical absorption spectroscopy Vishal Kumar et al. [27] have investigated the crystallization properties of \(40\text{SiO}_2-30\text{BaO}-20\text{B}_2\text{O}_3-10\text{A}_2\text{O}_3\) (A = Y, La, Al, Cr) and concluded that sample containing Cr\(_2\text{O}_3\) was not converted to glass completely. In the composition of \(40\text{SiO}_2-20\text{B}_2\text{O}_3-30\text{CaO}-10\text{M}_2\text{O}_3\) (M = Al, Cr, Y and La) glasses, Singh et al. [28] stated that M\(_2\text{O}_3\) plays crucial role in controlling the chemical durability and bioactivity of the glasses. Shao-Yi Wu et al. [29] have estimated the g factors and investigated the local structure for Cr\(^{5+}\) within Cr\(_2\text{O}_3\) nanocrystals embedded in the silica glass matrix by theoretical studies with the perturbation formulas and enhanced 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. Lilia C. Courrol et al. [30] have revealed the reduction of mechanical stresses and production of color centres (after laser irradiation) in ZBLAN (52ZrF$_4$–19BaF$_2$–4AlF$_3$–20NaF–(5–x)LaF$_3$: xCr$_2$O$_3$) glass with the presence of 1 mol% of chromium ions. Fouad El-Diasty et al. [31] correlated these properties with the structure and the presence of nonbridging oxygen ions in these glasses. A review of the fundamentals and recent research advances in optical properties of oxide glasses containing chromium has been reported by Manal Abdel-Baki and Fouad El-Diasty [32]. U.R. Rodríguez-Mendoza et al. [33] have elucidated the absorption and emission spectra of the Cr$^{3+}$ ions in tantalum tellurite glasses considering the Cr$^{3+}$ ions in an octahedral (Oh) environment. Raghavaiah and Veeraiah [34] have analyzed the dielectric and spectroscopic properties of 40PbO–(60–x)Sb$_2$O$_5$–xAs$_2$O$_3$: 0.4Cr$_2$O$_3$ (with x ranging from 10 to 55 mol%) and disclosed that lower concentrations of As$_2$O$_3$ are more favourable environments for the presence of larger concentrations of laser-emitting Cr$^{3+}$ ions in the composition. Zakharov [35] and Landry [36] have also investigated the ESR of Cr$^{3+}$ in phosphate glass; based on spin Hamiltonian they have evaluated the energy levels of the Cr$^{3+}$ paramagnetic ion. Van Die et al. [37] have analyzed the absorption, luminescence and decay mechanisms of chromium ions in germinate glasses; they have reported high quantum luminescence efficiency (the upper limit being 25%) for chromium ions.

Baiocchi et al. [38] have studied the optical and magnetic properties of chromium doped lead silicate glasses. They have assigned the bands observed in
the optical absorption spectrum to the appropriate transitions using Tanabe–Sugano diagrams. From the studies they have concluded that chromium ions exist in two oxidation states viz., \( \text{Cr}^{3+} \) and \( \text{Cr}^{6+} \) states with octahedral and tetrahedral coordinations respectively. Adam et al. [39] have investigated Fano antiresonances in the absorption spectra of heavy metal fluoride glasses doped with \( \text{Cr}^{3+} \) with an emphasis on the study of \( ^4A_2 \rightarrow ^2E, ^4T_2, ^2T_1 \) transitions. They have established a good agreement between the experimental absorption spectrum and the energy levels determined from the Tanabe-Sugano diagram of \( \text{Cr}^{3+} \) ions in these glasses.

4.3 Characterization

4.3.1 X-Ray diffraction

As glassy or amorphous materials do not have long-range order, a diffraction pattern containing sharp peaks is not expected as in crystalline materials. The X-ray diffraction spectra of C0, C1 and C4 glasses are shown in Fig. 4.1. No sharp Bragg peaks are observed in the spectra which indicate the amorphous nature of the glasses. However, a small hump in the spectra reveals the short range order of the glass samples.

4.3.2 Physical parameters

The physical parameters such as chromium ion concentration \( N_i \), mean chromium ion separation \( r_i \), polaron radius \( r_p \) and molar volume \( V_m \) are evaluated and mentioned in Table 4.1 along with the refractive indices of glasses.
Fig. 4.1 X-ray diffraction pattern of Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$: Cr$_2$O$_3$ glasses.

The measured density of chromium free sample is found to be 3.564 g/cm$^3$ and is found to increase with increase in the dopant concentration. A similar trend in refractive index and a reverse trend in molar volume of samples are noticed and recorded in Table 4.1. Among all the prepared glass samples the maximum value of density is 3.621 g/cm$^3$ for C5 glass.
Table 4.1 The density $\rho$, average molecular weight $M$, molar volume $V_m$, chromium ion concentration $N_i$, mean chromium ion separation $r_i$, polaron radius $r_p$, and refractive index $\mu$ of Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$: Cr$_2$O$_3$ glasses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho$ (g/cm$^3$)±0.001</th>
<th>$M$ (g/mol)±0.001</th>
<th>$V_m$ (cm$^3$/mol)±0.001</th>
<th>$N_i \times 10^{21}$ (ions/cm$^3$)±0.001</th>
<th>$r_i$ (Å)±0.001</th>
<th>$r_p$ (Å)±0.001</th>
<th>$\mu$±0.001</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0</td>
<td>3.564</td>
<td>103.234</td>
<td>28.964</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.682</td>
</tr>
<tr>
<td>C1</td>
<td>3.575</td>
<td>103.244</td>
<td>28.878</td>
<td>2.086</td>
<td>7.827</td>
<td>3.155</td>
<td>1.688</td>
</tr>
<tr>
<td>C3</td>
<td>3.599</td>
<td>103.283</td>
<td>28.699</td>
<td>10.493</td>
<td>4.568</td>
<td>1.841</td>
<td>1.696</td>
</tr>
</tbody>
</table>

4.4 Results

4.4.1 Optical absorption

Fig. 4.2 shows the optical absorption spectra of Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$ glasses added with different concentrations of Cr$_2$O$_3$, at room temperature in the wavelength range 250-850 nm. No absorption peaks are found in the spectrum of pure sample C0 as it is radical free. When chromium ions are incorporated in the glass system then the spectra exhibit two intense absorption bands, with band positions at 438 nm (22831 cm$^{-1}$), 625 nm (16000 cm$^{-1}$). Besides this another three feeble bands are identified at 351 nm (28490 cm$^{-1}$), 644 nm (15528 cm$^{-1}$) and 691 nm (14472 cm$^{-1}$). All these bands are noticed to shift to higher wavelength side. The intensity of the bands at 438 and 625 nm is observed to increase with increase in dopant concentration. The fundamental absorption edge reveals the band structure around the energy gap.
Fig. 4.2 Optical absorption spectra of chromium doped Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$ glasses at room temperature.

The absorption edge at 299 nm for C0 glass is red shifted to 342 nm (C5 glass) with gradual increase in concentration of chromium ions. Optical energy band gap $E_g$ of the glasses is determined from the Tauc plots drawn between $hv$ and $(\alpha hv)^{1/2}$ by extrapolating the linear region to $x$-axis where $(\alpha hv)^{1/2} = 0$ as shown in Fig. 4.3. The gradual decrease in optical band gap is noticed with increase in the concentration of Cr$_2$O$_3$. The optical band gap is observed to be high for C0 glass (4.29 eV) and low for C5 glass (3.37 eV).
\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Tauc plots of chromium doped Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$ glasses.}
\end{figure}

\begin{table}
\centering
\caption{Cut off wavelength (\(\lambda_c\)), absorption band positions, optical band gap (\(E_g\)), Urbach energy (\(\Delta E\)) and theoretical optical basicity (\(\Lambda_{th}\)) of the Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$: Cr$_2$O$_3$ glasses.}
\begin{tabular}{cccccccccc}
Glass & \(\lambda_c\) (nm) & Positions of transitions in nm from $^4A_{2g}(F)$ to & $^4T_{1g}(P)$ & $^4T_{1g}(F)$ & $^4T_{2g}(F)$ & $^2T_{1g}(G)$ & $^2E_g(G)$ & \(E_g\) (eV) & \(\Delta E\) (eV) & \(\Lambda_{th}\) ±0.0001 \\
\hline
C0 & 299 & - & - & - & - & - & - & 4.29 & 0.254 & 0.4474 \\
C1 & 315 & 351 & 438 & 625 & 644 & 691 & - & 4.02 & 0.481 & 0.4480 \\
C2 & 322 & 362 & 439 & 622 & 646 & 694 & - & 3.94 & 0.518 & 0.4493 \\
C3 & 328 & 365 & 435 & 624 & 649 & 690 & - & 3.66 & 0.528 & 0.4506 \\
C4 & 335 & 367 & 438 & 626 & 650 & 690 & - & 3.59 & 0.575 & 0.4524 \\
C5 & 342 & 368 & 439 & 628 & 652 & 691 & - & 3.37 & 0.602 & 0.4537 \\
\end{tabular}
\end{table}
Fig. 4.4. ln(α) versus photon energy (hν) of Cr₂O₃ doped Li₂O-PbO-B₂O₃-P₂O₅ glasses. Inset shows the variation of optical band gap (E₉) and Urbach energy (ΔE) with concentration of Cr₂O₃.

Urbach energy (ΔE) which gives the crucial information about the density of energy states in the band gap is evaluated from the plots drawn between photon energy hν versus ln α(ν) values. The relation between α(ν) and Urbach energy (ΔE) is given by the Urbach law as follows [40].

\[
α(ν) = C \exp(hν/ΔE)
\]  \hspace{1cm} (4.1)

Where C is a constant and ΔE is the Urbach energy interpreted as the energy gap between localized tail states in the forbidden region. ΔE values are acquired by taking the reciprocals of the slopes of the linear region of the ln α(ν) versus hν plots as shown in Fig. 4.4. The evaluated ΔE values which are found to increase
with the concentration of chromium ions are mentioned in Table 4.2. The minimum and maximum values of $\Delta E$ for C0 and C5 glasses are 0.2536 eV and 0.6015 eV respectively. Inset of Fig. 4.4 shows the variation of optical band gap and Urbach energy with concentration of dopant.

Theoretical optical basicity values of all glasses are evaluated by Eq. (4.2) [41] and included in Table 4.2.

$$\Lambda_{th} = \sum_{i=1}^{n} \frac{Z_i r_i}{|Z_0| \gamma_i}$$  \hspace{1cm} (4.2)

Where ‘$n$’ is the number of cations present, $Z_i$ is the oxidation number of $i^{th}$ cation, $r_i$ is the ratio of the number of $i^{th}$ cation to the number of oxides present, $Z_0$ is oxidation number of oxide and $\gamma_i$ is the basicity moderating parameter of the $i^{th}$ cation. $\gamma_i$ values are calculated using Eq. 4.3 [42].

$$\gamma_i = 1.36(x_i - 0.26)$$  \hspace{1cm} (4.3)

Where ‘$x_i$’ is Pauling electro negativity of cation. The optimum value of optical basicity is 0.4474 for C0 system and observed to increase with increase in content of chromium ions and its maximum value is 0.4537 for M6 glass matrix.

4.4.2 ESR spectra

The ESR spectra of Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$: Cr$_2$O$_3$ glasses recorded at room temperature are shown in Fig. 4.5. As there is no paramagnetic impurity in an undoped (C0) glass, no ESR signal is detected. When the pure glass is doped with different concentrations of Cr$_2$O$_3$ the spectrum of each glass gives two resonance signals. The spectrum exhibits a weak, low field resonance signal with effective g
value centered at 5.23 and a strong high field resonance signal at 1.986. The intensity of the two signals is found to increase with hike in the concentration of chromium ions but no change in g values is noticed.

![ESR spectra](image)

**Fig. 4.5** ESR spectra of Cr$_2$O$_3$ doped Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$ glasses at room temperature.

### 4.4.3 FTIR spectra

The structural analysis of Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$: Cr$_2$O$_3$ glasses are apprehended by infrared spectroscopy in the wavenumber range 400-1250 cm$^{-1}$.

The band positions and their respective assignments are furnished in Table 4.3. The infrared spectra of the samples are shown in Fig. 4.6. The spectrum of pure
sample shows the absorption bands at 1193 cm$^{-1}$ (identified due to the stretching vibrations of triangular BO$_3$ structural units), 1108 cm$^{-1}$ (assigned to PO$_2^-$ symmetrical stretching vibrations), 1029 cm$^{-1}$ (attributed to stretching vibrations of tetrahedral BO$_4$ units), 926 cm$^{-1}$ (due to P-O-P asymmetric vibrations), 779 cm$^{-1}$ (due to P-O-P symmetric vibrations), 694 cm$^{-1}$ (due to B-O-B bending vibrations) and 451 cm$^{-1}$ (vibrations due to PbO$_4$ structural units). Two new bands are identified due to the doping of Cr$_2$O$_3$ at 882 and 431 cm$^{-1}$ due to $\nu_3$-vibrations of CrO$_4^{2-}$ structural units and $\nu_4$ vibrations of Cr$_2$O$_3$ units respectively. Due to the addition of chromium ions to the pure glass matrix, the intensity of the bands due to BO$_3$ structural units, P-O-P asymmetric vibrations, B-O-B bending vibrations and vibrations of Cr$_2$O$_3$ units is observed to increase with a shift in the band position towards higher wavenumber. A reverse trend is noticed for the bands assigned to PO$_2^-$ symmetrical stretching vibrations, stretching vibrations of tetrahedral BO$_4$ units, $\nu_3$-vibrations of CrO$_4^{2-}$ structural units and vibrations due to PbO$_4$ structural units shifting the band position towards lower wavenumber. Interestingly the band due to P-O-P symmetric vibrations is blue shifted with a fall in the intensity of the band.

4.4.4 Dielectric properties

The values of $\varepsilon'$ and $\tan\delta$ at lab temperature (303 K) of C0 glass at 500 kHz are measured to be 3.25 and 0.008 respectively; these values are decreased significantly with increase in frequency.
**Fig. 4.6** IR spectra of chromium ions doped Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$ glasses at room temperature.

**Table 4.3** Summary of the data on various absorption band positions in the IR spectra (with a probable resolution of ±0.5 cm$^{-1}$) of the Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$: Cr$_2$O$_3$ glasses.

<table>
<thead>
<tr>
<th></th>
<th>C0</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-</td>
<td>431</td>
<td>432</td>
<td>435</td>
<td>438</td>
<td>444</td>
<td>$\nu_4$-Cr$_2$O$_3$ structural units</td>
</tr>
<tr>
<td></td>
<td>451</td>
<td>449</td>
<td>447</td>
<td>445</td>
<td>441</td>
<td>438</td>
<td>Vibrations due to PbO$_4$ structural units</td>
</tr>
<tr>
<td></td>
<td>694</td>
<td>678</td>
<td>692</td>
<td>695</td>
<td>695</td>
<td>697</td>
<td>B-O-B bending vibrations</td>
</tr>
<tr>
<td></td>
<td>779</td>
<td>792</td>
<td>782</td>
<td>785</td>
<td>782</td>
<td>782</td>
<td>P-O-P symmetric vibrations</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>882</td>
<td>881</td>
<td>867</td>
<td>850</td>
<td>-</td>
<td>$\nu_3$-vibrations of CrO$_4^{2-}$ structural units</td>
</tr>
<tr>
<td></td>
<td>926</td>
<td>922</td>
<td>925</td>
<td>927</td>
<td>927</td>
<td>929</td>
<td>P-O-P asymmetric vibrations</td>
</tr>
<tr>
<td></td>
<td>1029</td>
<td>1024</td>
<td>1032</td>
<td>1025</td>
<td>1034</td>
<td>1027</td>
<td>Stretching vibrations of B-O bonds in BO$_4$ units from tri, tetra and penta borate groups</td>
</tr>
<tr>
<td></td>
<td>1108</td>
<td>1099</td>
<td>1104</td>
<td>1105</td>
<td>1104</td>
<td>1105</td>
<td>PO$_2^-$ symmetrical stretching</td>
</tr>
<tr>
<td></td>
<td>1189</td>
<td>1190</td>
<td>1193</td>
<td>1186</td>
<td>1182</td>
<td>1191</td>
<td>B-O stretch in BO$_3$ units from pyro and ortho borate groups</td>
</tr>
</tbody>
</table>
When pure glass is doped with increasing concentrations of Cr$_2$O$_3$ at room temperature the values of $\varepsilon'$ and tan\(\delta\) are found to increase at any frequency. Fig. 4.7 shows the temperature dependence of dielectric constant for different glass samples at 10 kHz. It is noticed that the rate of increase of $\varepsilon'$ with temperature increases with the concentration of Cr$_2$O$_3$. The inset shows the variation of dielectric constant with temperature at different frequencies for C2 glass matrix. The values of $\varepsilon'$ are observed to increase slowly up to about 353 K and beyond this temperature; they are noticed to increase sharply and highly frequency dependent with large values at lower frequencies. The same trend is witnessed for all the other glasses. The plots drawn between tan\(\delta\) versus temperature are also demonstrated the similar type of behavior as shown by $\varepsilon'$ versus temperature. The variation of dielectric loss with temperature at 1 kHz for different concentrations of Cr$_2$O$_3$ is shown in Fig. 4.8. The inset shows the variation of tan\(\delta\) with temperature at different frequencies for C5 glass. The plots of pure and chromium doped glasses have exhibited distinct maxima, with increase in frequency these maxima shift towards higher temperature, showing the dielectric relaxation character of dielectric loss of all the glasses under investigation. The variation of dielectric parameters ($\varepsilon'$ and tan\(\delta\)) at room temperature with different concentrations of chromium ions at 10 kHz is shown in Fig. 4.9.
Fig. 4.7 Variation of dielectric constant $\varepsilon'$ with temperature at 10 kHz frequency for different concentration of $\text{Cr}_2\text{O}_3$ in $\text{Li}_2\text{O-\text{PbO-B}_2\text{O}_3-P}_2\text{O}_5$ glasses. Inset shows the variation of dielectric constant with temperature at different frequencies of C2 glass system.

The observations on the variation of $\tan\delta$ with temperature for different concentrations of dopant indicate the gradual increase in the broadness and $\tan\delta_{\text{max}}$ of relaxation curves. Among all the prepared samples C5 glass has a maximum value of dielectric loss with a shift of the relaxation region towards lower temperature. The summary of data on relaxation effects of $\text{Li}_2\text{O-\text{PbO-B}_2\text{O}_3-P}_2\text{O}_5$: $\text{Cr}_2\text{O}_3$ glasses are mentioned in Table 4.4 along with the data, pertaining to activation energy for dipoles and breakdown strength [43].
Fig. 4.8 Variation of loss factor $\tan \delta$ with temperature at 1 kHz frequency for different concentrations of Cr$_2$O$_3$ in Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$ glasses. Inset of shows the variation of $\tan \delta$ with temperature at different frequencies for C5 glass.

Table 4.4 Summary of the data on loss factor of Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$: Cr$_2$O$_3$ glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>$(\tan \delta)_{\text{max}}$</th>
<th>Temp. region of relaxation (K)</th>
<th>Activation energy for dipoles $W_d$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0</td>
<td>0.058</td>
<td>385-436</td>
<td>3.587</td>
</tr>
<tr>
<td>C1</td>
<td>0.076</td>
<td>376-428</td>
<td>3.421</td>
</tr>
<tr>
<td>C2</td>
<td>0.115</td>
<td>368-423</td>
<td>3.258</td>
</tr>
<tr>
<td>C3</td>
<td>0.144</td>
<td>358-415</td>
<td>3.099</td>
</tr>
<tr>
<td>C4</td>
<td>0.188</td>
<td>350-411</td>
<td>2.944</td>
</tr>
<tr>
<td>C5</td>
<td>0.230</td>
<td>345-408</td>
<td>2.793</td>
</tr>
</tbody>
</table>

Using the relation $f = f_0 \exp (-W_d/KT)$ (4.4)

the activation energy $W_d$, for dipoles is evaluated. $W_d$ is observed to be maximum (3.587 eV) for C0 sample and minimum (2.793 eV) for C5 glass. The a.c. conductivity $\sigma_{\text{ac}}$ at different temperatures is calculated using the relation [43]
**Fig. 4.9** Variation of dielectric constant and loss factor with the concentration of Cr$_2$O$_3$ at 10 kHz at room temperature (303 K) for Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$ glasses.

**Table 4.5** Summary of data on ac conductivity $\sigma_{ac}$ for Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$: Cr$_2$O$_3$ glasses (at 303 K).

<table>
<thead>
<tr>
<th>Glass</th>
<th>$\sigma_{ac}$ ($x 10^6$) ($\Omega$-cm)$^{-1}$</th>
<th>N(E$_F$) in ($x 10^{25}$ eV$^{-1}$/cm$^3$)</th>
<th>Activation energy for conduction eV</th>
<th>Breakdown strength kV/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Austin and Mott</td>
<td>Butcher and Hyden</td>
<td>Pollak</td>
<td></td>
</tr>
<tr>
<td>C0</td>
<td>8.46</td>
<td>28.05</td>
<td>11.69</td>
<td>28.49</td>
</tr>
<tr>
<td>C1</td>
<td>9.75</td>
<td>30.11</td>
<td>12.56</td>
<td>30.58</td>
</tr>
<tr>
<td>C2</td>
<td>11.04</td>
<td>32.04</td>
<td>13.36</td>
<td>32.54</td>
</tr>
<tr>
<td>C3</td>
<td>12.91</td>
<td>34.65</td>
<td>14.45</td>
<td>35.19</td>
</tr>
<tr>
<td>C4</td>
<td>15.88</td>
<td>38.43</td>
<td>16.02</td>
<td>39.03</td>
</tr>
<tr>
<td>C5</td>
<td>18.73</td>
<td>41.73</td>
<td>17.40</td>
<td>42.37</td>
</tr>
</tbody>
</table>
**Fig. 4.10** Variation of a.c. conductivity $\sigma_{ac}$ with $1/T$ for different glasses at frequency 100 kHz. Insets (a) and (b) gives the dependence of activation energy (A.E) for conduction and $\sigma_{ac}$ on the concentration of the Cr$_2$O$_3$ respectively at 100 kHz.

$$\sigma_{ac} = \omega \varepsilon\varepsilon_0 \tan \delta$$  \hspace{1cm} (4.5)

Here $\varepsilon_0$ is the dielectric constant of vacuum. The variation of $\sigma_{ac}$ with $1/T$ for pure and doped glasses at 100 kHz is shown in Fig. 4.10. Using these plots, the activation energy for conduction, in the high temperature region over which a near linear dependence of log $\sigma_{ac}$ with $1/T$ could be observed, is evaluated and furnished in Table 4.5.
The activation energy for conduction is found to be the lowest (0.121 eV) for C5 glass and the maximum value of activation energy for conduction is 0.166 eV for C0 glass. The inset (a) shows the variation of activation energy for conduction for different concentrations of chromium ions at 100 kHz. From this figure it is seen that the activation energy for conduction decreases with increase in chromium ion concentration. Inset (b) indicates the variation of $\sigma_{ac}$ with the concentration of dopant at 100 kHz. Fig. 4.11 shows the plot of $\sigma_{ac}$ versus 1/T at different frequencies for C3 glass. From the graphs it is concluded that $\sigma_{ac}$
increases with increase in frequency. The inset shows the variation of $\sigma_{ac}$ with activation energy for conduction at 473 K. A near linearity is found between $\sigma_{ac}$ and activation energy for conduction.

The measured value of dielectric breakdown strength of C0 glass at room temperature is 15.42 kV/cm. The value is observed to decrease with increase in the concentration of chromium ions and reaches the minimum value of 13.95 kV/cm for C5 glass. These values are presented in Table 4.5.

4.5 Discussion

4.5.1 Physical parameters

Normally density of solids is a wonderful tool for analyzing the structural changes. Density is influenced by structural compactness, variation in geometrical configuration, cross link density, coordination number and dimensions of interstitial vacancies of the glass system [44]. The increase in density due to doping of Cr$_2$O$_3$ is proposed due to the replacement of lighter cation P$^{5+}$ by heavier Cr$^{3+}$ ion showing that the density of a sample is very much sensitive to the atomic weight and ionic size [45]. The maximum value of density and minimum molar volume of C5 glass reveal the compact nature of the specimen. When the basic glass is doped with Cr$_2$O$_3$, the chromium ions occupy the interstices of the glass network by creating B-O-Cr and Pb-O-Cr linkages, in sequence with conversion of BO$_4$ tetrahedral to BO$_3$ triangular structural units. The ionic radii of B$^{3+}$ in BO$_4$ units (0.25 Å) are higher than B$^{3+}$ in BO$_3$ units (0.15 Å) [46,47].
4.5.2 Optical absorption

Optical absorption spectra of the glass samples exhibit two prominent absorption peaks at 438 and 625 nm. These two bands have been identified due to transitions of Cr\(^{3+}\) (d\(^3\)) ions; using Tanabe-Sugano diagrams the spectrum has been analyzed and the bands are attributed to \(^4\text{A}_2\) (F) \(\rightarrow\) \(^4\text{T}_1\) (F), \(^4\text{A}_2\) (F) \(\rightarrow\) \(^4\text{T}_2\) (F) transitions respectively. Interestingly, two weak, narrow bands at 644 and 691 nm due to spin and parity forbidden transitions \(^4\text{A}_2\) (F) \(\rightarrow\) \(^2\text{T}_1\) (G) and \(^4\text{A}_2\) (F) \(\rightarrow\) \(^2\text{E}_g\) (G) respectively have been located on \(^4\text{T}_2\) band in the spectra of as prepared glasses. These bands appear due to spin orbit interaction and mixing between \(^2\text{E}\) and \(^4\text{T}\) and \(^2\text{T}_1\) and \(^4\text{T}_2\) levels [48]. The increase in widths of \(^2\text{T}_1\) and \(^2\text{E}\) bands has been noticed with increase in the concentration of chromium ions. This increase in width indicates an increasing degree of disorder in the glass system, may be due to the increasing concentration of induced heterogeneous nucleation centers in the glass samples. This result can also be explained as follows: as the concentration of Cr\(^{3+}\) ions increases in the glass network, there is a possibility for the coupling of Cr\(^{3+}\) ions with the Cr\(^{6+}\) ions. This type of coupling makes the transitions spin allowed and responsible for increase in the intensity of these bands [49]. A new band is identified at 351 nm due to Cr\(^{6+}\) ions [50]. The Cr\(^{6+}\) ions exist in the form of Cr\(^{6+}\)O\(^2-\) centers in the frame of CrO\(_4\)\(^2-\) groups [51]. Cr\(^{6+}\) ion belongs to d\(^0\) closed shell and does not have electrons in d shell. The Cr\(^{5+}\) ions are expected to show absorption band around 465 nm [52]; but such band is not observed in the spectra.
of the present glasses. Therefore concentration of Cr$^{5+}$ ions in the present glass matrices seems to be insignificant.

The increase in the intensity of $^4T_1$ and $^4T_2$ absorption bands and a simultaneous minute increase in the intensity of the band at 351 nm in the spectra of all the glasses from C1 to C5 indicate an increase in the concentration of Cr$^{3+}$ ions with the Cr$^{6+}$ ions in the present investigation. The increase in the area of the curves due to the bands at 439 and 628 nm are much greater than the increase in area of the curve due to the band at 351 nm. This clearly indicates large increase in the concentration of Cr$^{3+}$ ions than the Cr$^{6+}$ ions. The Cr$^{6+}$ ions participate in the glass network with CrO$_4^{2-}$ structural units and alternate with BO$_4$ units, leading to a decrease in the disorder of the glass network [50]. In the present study effect of Cr$^{3+}$ ions is dominating Cr$^{6+}$ ions. Higher the concentration of Cr$^{3+}$ ions simultaneously higher is the concentration of non-bridging oxygens (NBO) in the glass matrix. The presence of higher concentration of these donor centers decreases the optical band gap and shifts the absorption edge towards higher wavelength side as observed for the glasses C1 to C5.

The observed maximum Urbach energy for C5 glass (0.6015 eV) indicates the maximum width of the tails among investigated samples. The increase in Urbach energy ($\Delta E$) with increase in the concentration of Cr$_2$O$_3$ is expected due to formation of defects like fluctuations in bond angle distortions and dangling bonds [53]. The additional factor contributing to the edge broadening is a static disorder which increases the density of localized states $N(E_F)$ of these defects.
The optical basicity ($\Lambda_{th}$) of a chemically complex glass is the mean polarization condition of the ligands ($O^{2-}$) and their mean ability to transfer fractional charges to central cation [54]. Increase in $\Lambda_{th}$ reveals the increase of localized donor pressure on cations of glass matrix which in turn increases the ionic nature of the glass. Duffy and Ingram [55] proved that the polarizability of oxygen ions is directly proportional to the optical basicity. The hike in the polarizability of oxygen ions is the evidence for the raise in the concentration of NBOs [56]. This is supported by the observed increase in $\Delta E$ and decrease in $E_g$ values.

4.5.3 ESR spectra

The magnetic properties of Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$: Cr$_2$O$_3$ glasses are due to Cr$^{3+}$ ($3d^3$) paramagnetic ions. As per Hund’s rule the ground state of chromium ions is $^4F$ which is associated with $3d^3$ electronic configurations. In an octahedral crystal field, this state splits into an orbital singlet $^4A_{2g}$ and two more orbital triplets $^4T_{1g}$ and $^4T_{2g}$ [57]. In a distorted octahedral site, the electronic levels can be described by a spin-Hamiltonian [58].

$$H = g\beta BS + D \left[ S_z^2 - \frac{1}{3} (S(S+1)) \right] + E \left( S_x^2 - S_y^2 \right)$$ (4.6)

Here the first term represents the electronic Zeeman term; second term represents the zero-field splitting of the quartet ground state. In the absence of an external magnetic field $B$; the four fold spin degeneracy of the $^4A_{2g}$ state is removed by a subsequent low symmetric field resulting in a zero field splitting of the Kramer’s doublets $|\pm 3/2>$ and $|\pm 1/2>$ even at zero field. In the presence of magnetic field,
the degenerate doublets split further and more transitions are possible. However, the number of resonance signals observed due to transitions depends upon the magnitude of the zero fields splitting for a given photon energy [59].

The ESR spectra of the glasses exhibit two intense resonance signals at $g = 1.986$ and 5.23 due to Cr$^{3+}$ ions [24,60]. According to Landry, the low field line at $g = 5.23$ is attributed to the isolated Cr$^{3+}$ ions that have local rhombic sites subjected to strong crystal field effects [61,62]. This signal arises mainly due to $-3/2 \leftrightarrow +3/2$, that are allowed due to low symmetry of Cr$^{3+}$ ions. The larger intensity of this low field peak exhibited by the spectrum of all glasses indicates higher concentrations of isolated Cr$^{3+}$ ions in the samples. The resonance signal in the high field region with $g = 1.986$ arises due to exchange coupled Cr$^{3+}$ - Cr$^{3+}$ pairs [63]. The intensity and line width of this signal are found to increase with increase in concentration of nucleating agent. This indicates the large increase in the concentration of Cr$^{3+}$ ions in the present glasses. The higher concentration of Cr$^{3+}$ ions which act as glass modifiers enhances the concentration of NBOs in the glass matrix. These donor centers reduces the optical band gap of the glasses as discussed in optical absorption studies. If there is a large separation between two Kramer’s doublets then a resonance signal at $g = 2.6$ is observed. As there is no large separation between two Kramer’s doublets so the resonance signal at $g = 2.6$ is not observed [64].
4.5.4 FTIR Spectra

The structural changes in Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$: Cr$_2$O$_3$ glasses are investigated by analyzing the FTIR spectra in the wavenumber range 400-1250 cm$^{-1}$. When Li$_2$O is incorporated in B$_2$O$_3$ it leads to conversion of sp$^2$ planar BO$_3$ units into more stable sp$^3$ tetrahedral BO$_4$ units [65,18]. Long tetrahedral chains of BO$_4$ are formed when each BO$_4$ unit is bonded with two other similar units. However, when PbO is added to the glass system tetrahedral BO$_4$ units are converted into triangular BO$_3$ units, by forming PbO$_n$ polyhedron when it is surrounded by BO$_4$ tetrahedrons. This structure behaves like a defect in the glass network [66]. When the pure glass is doped with Cr$_2$O$_3$, it will twist or distort the interconnected chains of BO$_4$ units and enhance the randomness of glass network.

With the increasing concentration of Cr$_2$O$_3$ the intensity of vibration band corresponding to BO$_3$ units, P-O-P asymmetric vibrations and B-O-B bending vibrations increases [67-70]. This clearly suggests the escalating modifying action of Cr$^{3+}$ ions with the increasing content of Cr$_2$O$_3$. The significant decrease in the intensity of the bands due to PO$_2^-$ symmetrical stretching, BO$_4$ units and P-O-P symmetric vibrations with increase in the concentration of nucleating agent indicates the decline in the Cr$^{6+}$ ions which act as glass formers. The intensity of the band due to $v_4$ vibrations of Cr$_2$O$_3$ with CrO$_6$ octahedral units increases where as the intensity of the band due to CrO$_4^{2-}$ tetrahedral units follows the reverse trend. These features confirm the raise of CrO$_6$ octahedral units at the expense of CrO$_4^{2-}$ tetrahedral units [16,18,71]. The increase in modifying action of Cr$_2$O$_3$ may
rupture the BO$_4$, P-O-P, P=O and PbO$_4$ bonds with the creation of NBOs and creates structural disorder in the glasses. In compliance with the structural changes inferred from FTIR studies, the observed decrease in band gap, increase in Urbach energy and increase in ESR signal intensity induced by doping of Cr$_2$O$_3$ in the glass network might be explained by the increase of BO$_3$ and CrO$_6$ structural units along with the increase of NBOs (with increase of B-O’ bonds).

4.5.5 Dielectric properties

The influence of temperature on dielectric properties of glasses is a complicated phenomenon. The electronic, ionic, dipolar and space charge polarizations are the main sources of dielectric constant in glasses. Among these, the space charge polarization depends on the purity and the perfection of the glasses. In the present discussion on dielectric properties of Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$ glasses, with the increase in the concentration of Cr$_2$O$_3$ the values of $\varepsilon'$, tan$\delta$ and $\sigma_{ac}$ are found to increase at any frequency and temperature. The values of breakdown strength and activation energy for ac conduction are found to decrease with increase in content of dopant. This result is expected due to the gradual conversion of Cr$^{6+}$ ions (network formers) into Cr$^{3+}$ ions which act as modifiers (proved from ESR and optical absorption spectra). These ions depolymerize the glass matrix and create bonding defects by breaking B-O, B-O-Pb etc. bonds. These defects create easy path ways for the migration of charges that would build up space charge polarization and causes the increase in the dielectric parameters [72-75].
The ascending values of $\tan \delta_{\text{max}}$ and narrowing of relaxation peaks with increase in chromium ions indicate an increase of freedom for dipoles to orient in the field direction, obviously due to decrease in the rigidity of the glass matrix. In general, the dielectric relaxation effects are observed only when the metal ions present in the glass system are in divalent state as discussed earlier [71,76]. The divalent ions of lead together with a pair of any cationic vacancies may form dipoles and such dipoles are responsible for the observed dielectric relaxation effects. Indirectly, it leads to the conclusion that there is decrease in rigidity of the glass network at higher concentrations of $\text{Cr}_2\text{O}_3$.

In the present discussion of the glass samples, in the high temperature region the conduction phenomenon can be explained on the basis of defect model suggested by Ingram [77]. When a plot is drawn between $\log \sigma(\omega)$ and activation energy for conduction a near linear relationship is observed (inset of Fig. 4.11). An approximate linearity between the conductivity and the activation energy reveals the fact that conductivity enhancement is directly proportional to the increasing mobility of the charge carriers in the high temperature region. Since the $\text{Pb}^{2+}$ ions are less mobile than the alkali ions: $\text{Pb}^{2+}$ ions can be regarded as virtually immobile within the time window of hopping processes of $\text{Li}^+$ ions [78]. Therefore in the high temperature region, the mono valent lithium ions contribute to the conduction in the present samples. Hence, the conductivity is found to increase with increase in the concentration of $\text{Cr}_2\text{O}_3$ due to increase in the modifying action of $\text{Cr}^{3+}$ ions. The highest conductivity and the lowest activation energy obtained
for C5 glass are obviously due to the highest concentration of the Cr\(^{3+}\) ions; which may find easy paths for migration in the disordered glass network. The proportionate higher concentration of Cr\(^{6+}\) ions takes network forming positions which restrict the mobility of Li\(^{+}\) ions and hence the conductivity is found to decrease for lower concentration of Cr\(_{2}\)O\(_{3}\) in the glasses.

Among different types of conduction mechanisms in the glasses (such as band conduction, conduction in extended states, conduction in localized states near the band edge and conduction in localized states near the Fermi level), the conduction in the localized states near the Fermi level takes place when ac conductivity is nearly temperature independent and varies linearly with frequency. The conduction in the present Li\(_{2}\)O-PbO-B\(_{2}\)O\(_{3}\)-P\(_{2}\)O\(_{5}\): Cr\(_{2}\)O\(_{3}\) glasses in the low temperature region (up to nearly 340 K) can safely be attributed to take place by this mechanism. The value of density of energy states N(E\(_{F}\)) near Fermi level, for 100 kHz frequency and at 303 K is evaluated on the basis of quantum mechanical tunneling model \[79,80\] as per the procedure given in the papers \[72,81,82\] and is furnished in Table 4.5. The value of N(E\(_{F}\)) is found to increase with increase in concentration of chromium ions, indicates an increase in the disorder of the glass system and is supported by the increase of Urbach energy ΔE values at higher concentrations of dopant in the glass matrix. The value of N(E\(_{F}\)) is found to be maximum for C5 glass.

A gradual decrease in the dielectric breakdown strength (from that of the pure glass) of glasses has been observed when the concentration of Cr\(_{2}\)O\(_{3}\) is
increased. When an electric field is applied to the dielectric, the heat of dielectric loss is liberated. If the applied electric field (E) is an alternating field, the specific dielectric loss, i.e. the loss per unit volume of the dielectric is given by the following equation [83].

\[ \rho_1(W/m^3) = E^2 \omega \epsilon' \epsilon_o \tan \delta \] (4.7)

Where E is the strength of applied electric field. This equation indicates that the higher the values of \( \epsilon' \tan \delta \) of the glass at a given frequency, the higher are the values of \( \rho_1 \). When a voltage is applied across a dielectric, heat is liberated, then the temperature of the dielectric increases and loss increases further more. The dielectric breakdown strength is, in fact, inversely proportional to the specific dielectric loss given by Eq. (4.7).

The observations on dielectric breakdown strength of Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$: Cr$_2$O$_3$ glasses, as mentioned earlier, indicate the rate of increase of \( \epsilon' \tan \delta \) with temperature as the highest for C5 glass. The heat liberated during the breakdown achieved by the application of voltage across the dielectric raises the \( \epsilon' \tan \delta \) value. The dielectric breakdown strength is inversely proportional to \( \epsilon' \tan \delta \) [62]. Thus the dielectric breakdown strength is lowest for the glass C5 when compared to the other glasses [Table 4.5]. Hence, the results on dielectric breakdown strength of Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$: Cr$_2$O$_3$ glasses revealed that there is a maximum internal disorder in the C5 glass.
4.6. Conclusions

The summary of conclusions drawn from the study of various properties of Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$: Cr$_2$O$_3$ glasses is mentioned below:

i) Glasses with composition 20Li$_2$O-20PbO-45B$_2$O$_3$-(15-x) P$_2$O$_5$: xCr$_2$O$_3$ (x ranging from 0 to 1mol %) were synthesized with conventional melt quenching and heat treatment.

ii) The absence of Bragg peaks in the XRD spectra of the prepared samples revealed the amorphous nature of the glasses.

iii) The increase in intensity of optical absorption bands of 438 and 625 nm is attributed to the increase in concentration of Cr$^{3+}$ ions occupying the octahedral positions in the glass network.

iv) The decrease in optical band gap and the gradual increase in Urbach energy with the increasing content of dopant is due to the increase of Cr$^{3+}$ ions and the increase in density of localized state.

v) The observed hike in optical basicity of the glasses with the increasing content of Cr$_2$O$_3$ showed the increase in ionic nature of the glasses.

vi) The ESR spectral analysis indicated that chromium ions are predominantly in the Cr$^{3+}$ state and occupy octahedral positions with increase in the dopant concentration. The concentration of such ions is found to be the maximum in C5 glass.

vii) IR spectra showed the increase in intensity of the bands due to BO$_3$, B-O-B, P-O-P asymmetrical and $\nu_4$-Cr$_2$O$_3$ structural units with increase
in the content of nucleating agent Cr$_2$O$_3$. This result indicated the increase of NBOs reducing the rigidity of the glass matrix.

vii) The dielectric parameters viz. $\varepsilon'$, Tanδ and $\sigma_{ac}$ are observed to increase whereas the dielectric breakdown strength and the activation energy for ac conduction are found to decrease from C0 to C5 glasses indicating an increase in the depolymerisation of the glass system due to the presence of increasing concentration of Cr$^{3+}$ ions that act as modifiers.
References


