Influence of valance states and co-ordination of cobalt ions on some physical properties of PbO–Bi$_2$O$_3$–As$_2$O$_3$: CoO glass system

The glasses of the composition (40-x) PbO–15 Bi$_2$O$_3$–45As$_2$O$_3$–x CoO, with 0 ≤ x ≤ 0.6 mol% in the steps of 0.1 were synthesized. The dielectric properties viz., dielectric constant, loss and ac conductivity over moderately larger ranges of frequency and temperature were investigated. The results were analyzed with the aid of the data on optical absorption, IR spectra. The analysis indicated that there is an increase in the insulating strength of the glasses with increase in the concentration of CoO up to 0.4 mol%.
Influence of valance states and co-ordination of cobalt ions on some physical properties of PbO–Bi$_2$O$_3$–As$_2$O$_3$: CoO glass system

5.1 Introduction

Cobalt ion is being extensively investigated in several commercial silica based glasses, glass ceramics and other crystalline dielectric materials [1-7]. The glasses containing cobalt ions are good candidates for non-linear optical absorbers, needed for passive modulations of laser beam [8]. These materials are also considered as the useful materials for Q-switching devices [9, 10], in view of the fact that they exhibit strong luminescence in the visible and near infrared regions. In the glasses, cobalt ions mainly exist in Co$^{2+}$ state. Co$^{2+}$ ions create color centers with absorption bands in the visible and NIR regions [11] and produce blue and pink glasses. The color of the glass depends on the Co$^{2+}$ content, its specific coordination (tetrahedral or octahedral), composition and basicity of the glass. Though, a reasonably good number of recent studies on the environment of cobalt ions by means of spectroscopic studies are available, majority of them are restricted mainly to silicate glasses. The structural probing of cobalt ions especially in the glass systems like PbO–Bi$_2$O$_3$–As$_2$O$_3$ is highly interesting to investigate since the electron phonon interaction between the bismuth-arsenate glass network and the cobalt ions is reported to be very strong with pronounced anharmonic effects [12].
The objective of this chapter is to synthesize PbO–Bi$_2$O$_3$–As$_2$O$_3$ glasses with small concentrations of CoO as dopant, to characterize by variety of techniques viz., XRD, DTA and energy dispersive spectra (EDS) and to throw some light on the environment of the cobalt ions in the glass network by studying their dielectric properties (viz., dielectric constant, dielectric loss, ac conductivity over a wide range of temperatures and frequencies) and spectroscopic properties (viz., optical absorption, IR).

A particular composition (40-x) PbO–15 Bi$_2$O$_3$–45As$_2$O$_3$–x CoO, with 0 ≤ x ≤ 0.6 mol% in the steps of 0.1 is chosen for the present study; the samples are labeled as Co$_0$ (x = 0), Co$_1$ (x = 0.1), Co$_2$ (x = 0.2), Co$_3$ (x = 0.3), Co$_4$ (x = 0.4), Co$_5$ (x = 0.5) and Co$_6$ (x = 0.6).

The details are as follows:

Co$_1$: 39.9 PbO–15 Bi$_2$O$_3$–45 As$_2$O$_3$: 0.1 CoO
Co$_2$: 39.8 PbO–15 Bi$_2$O$_3$–45 As$_2$O$_3$: 0.2 CoO
Co$_3$: 39.7 PbO–15 Bi$_2$O$_3$–45 As$_2$O$_3$: 0.3 CoO
Co$_4$: 39.6 PbO–15 Bi$_2$O$_3$–45 As$_2$O$_3$: 0.4 CoO
Co$_5$: 39.5 PbO–15 Bi$_2$O$_3$–45 As$_2$O$_3$: 0.5 CoO
Co$_6$: 39.4 PbO–15 Bi$_2$O$_3$–45 As$_2$O$_3$: 0.6 CoO
5.2 Brief review of the previous work on glasses containing cobalt ions

Studies on cobalt ions doped lead bismuth arsenate glasses are very rare. However, some of the recent studies on various glasses containing cobalt ions are briefly reviewed below:

Bhattacharya et al [13] have presented the effects of metalloids on the thermal stability and magnetic properties of (Fe,Co)-Mo-B-C-P-Si metallic glasses. Temperature-time transformation (TTT) studies and investigation of crystallization properties using transmission electron microscopy confirm the beneficial effect of cobalt on the thermal stability, rendering the present alloys promising for scientific study and soft magnet applications. Nagaraja et al [14] have reported the electrical conductivity studies in single and mixed alkali doped cobalt-borate glasses. They have analyzed these data in the light of Mott's Small Polaron Hopping (SPH) Model and evaluated various physical and polaron hopping parameters such as polaron hopping distance, polaron radius, polaron binding energy, polaron band width, polaron coupling constant, effective dielectric constant, density of states at Fermi level. Das et al [15] have prepared silver phosphate mixed with cobalt chloride and have measured the electrical conductivity of these samples. Bergo et al [16] have reported the dielectric properties of $\text{P}_2\text{O}_5$-$\text{Na}_2\text{O}$-$\text{Li}_2\text{O}$ glasses containing $\text{WO}_3$, $\text{CoO}$ or $\text{Fe}_2\text{O}_3$ at radio frequency (100 kHz) and in the microwave region (9 GHz). The difference among dielectric parameters (at 100 kHz and 9.00 GHz) was
attributed to the valence state of the transition metal ions in the glass structure, further they have concluded that the dielectric constant is lower in the microwave region, due to structural relaxation mechanisms. Thulasiramudu et al [17] have studied the optical characterization of Co$^{2+}$ ions doped zinc lead borate glasses. Their studies have indicated that the presence of both PbO and ZnO make these glasses to be good moisture-resistant optical systems. Optical and physical properties have been found to be more encouraging towards their use as novel luminescent optical materials. Khasa et al [18] have reported the effect of cobalt ions on the EPR and d.c. conductivity in vanadyl doped CoO-M$_2$O-B$_2$O$_3$ (M=Li, K) glasses. From these studies, they have concluded that addition of CoO to the sample exhibits a "blocking effect" on the overall mobility of alkali ions which causes the decrease in conductivity with increase in CoO:M$_2$O ratio. Kojima et al [19] have reported electron spin resonance spectra of high-spin Co$^{2+}$ doped in alkali borate and alkali germanate glasses measured at 4.2 K. On the basis of the spectral line shape, the observed spectra, they have classified spectra into four types that represent Co$^{2+}$ ions in octahedral coordination, a mixture of some types of coordination, tetrahedral coordination with nearly axial symmetry and distorted tetrahedral coordination. Lakshminarayana and Buddhudu [20] have reported spectroscopic properties of Mn$^{2+}$, Co$^{2+}$ and Ni$^{2+}$ in B$_2$O$_3$-ZnO-PbO glasses. In this study, they have reported red emission due to $^2$E($^2$G) $\rightarrow$ $^4$A$_2$(dF) tetrahedral transition of Co$^{2+}$
ions in this glass matrix. Ryba-Romanowski et al [21] have studied the optical spectra of chromium, vanadium and cobalt ions in lanthanum orthogallate crystals. In this study they have pointed out the cobalt ions exists in Co\(^{2+}\) and Co\(^{3+}\) ionic states. Mansour et al [22] have prepared CoO-TeO\(_2\)-V\(_2\)O\(_5\) glass system and have reported the results of studies on dc conductivity, density and molar volume.

El-Batal et al [23] have investigated the effects of glass composition and gamma rays irradiation on the optical and infrared absorption spectra of some selected ternary silicate glasses containing mixed CoO+NiO. They have interpreted experimental results by assuming that CoO and NiO exist mainly in the divalent state with possible tetra and octahedral coordinations. Mouhsine et al [24] have prepared two series of P\(_2\)O\(_5\) based oxide glasses containing both MoO\(_3\) and CoO oxides and investigated the infrared (IR) and electron paramagnetic resonance spectra. In their study, they have found that Co\(^{2+}\) ions exists mainly octahedral environment in both HS and LS forms and interpreted the result in term of a spin-crossover for Co(II) in these glasses. Möncke and Ehrt [25] have investigated the influence of cobalt and nickel on the formation of irradiation-induced defects was studied in fluoride, phosphate, silicate and borosilicate glasses. They have found that the irradiation produces more defects in Co\(^{2+}\) doped glasses than for Ni\(^{2+}\)-doped glasses and they have also reported that Co\(^{2+}\) was photooxidized to (Co\(^{2+}\))\(^+\) in all glasses. Esposito et al
[26] have synthesized cobalt-silicon mixed oxide materials (Co/Si=0.111, 0.250 and 0.428) starting from Co(NO$_3$)$_2$·6H$_2$O and Si(OCH$_3$)$_4$ using a modified sol-gel method and investigated the structural, textural and surface chemical properties were investigated by thermogravimetric/differential thermal analyses (TG/DTA), XRD, UV-vis, FT-IR spectroscopy of this material. In this study, they have found that the presence of cobalt affected the textural properties of the siloxane matrix by decreasing microporosity and increasing mesoporosity. Duan et al [27] have prepared transparent glass ceramics containing Co$^{2+}$:LiGa$_5$O$_8$ nanocrystals and reported two emission bands in the visible and near infrared (NIR) regions due to $^4$T$_1$($^4$P) → $^4$A$_2$($^4$F) and $^4$T$_1$($^4$P) → $^4$T$_2$($^4$F) transitions of tetrahedral Co$^{2+}$ respectively. Bhatty et al [28] have studied the optical absorption spectra of cobalt (II) in Tl$_2$O-B$_2$O$_3$ glasses and they have also been compared with those in binary alkali borate glasses. They concluded that in low thallium borate glasses cobalt (II) is octahedral while the concentration of tetrahedral cobalt (II) increases with increasing Tl$_2$O content of the glass. Denisov et al [29] have reported that Co:LiGaO is a saturable absorber passive Q switch for 1.34 μm Nd:YAlO and 1.54 μm Er:Glass lasers. Malyarevich et al [30] have also reported similar studies in magnesium-aluminum spinel nanocrystallites containing cobalt ions. These authors have measured the relaxation time of $^4$A$_2$ → $^4$T$_1$($^4$F) transition of Co$^{2+}$ ions as 450 ± 150 ns. Kim et al [31] have prepared cobalt (Co) and
tantalum (Ta) co-substituted BiFeO$_3$ polycrystalline ceramics and investigated the dielectric and magnetic properties. Sakuda et al [32] have fabricated solid-state lithium secondary batteries using LiCoO$_2$ particles coated with amorphous Li$_2$O-TiO$_2$ films as an active material and Li$_2$S-P$_2$S$_5$ glass ceramics as a solid electrolyte and investigated electrochemical performance. Magnetic susceptibility investigation of CoO–Bi$_2$O$_3$–GeO$_2$ glasses was carried out by Ardelean et al [33]. Nanostructures of sputtered thin films consisting of cobalt oxide and soda lime glass were analyzed by Yamamoto et al [34] by transmission electron microscope. In this, a relation between nanostructure and composition of the films, and a mechanism of formation of the nanostructures were discussed in terms of solvability of cobalt ion in the glass matrix.

The study on interaction of gamma rays with some sodium phosphate glasses containing cobalt ions is carried out by ElBatal et al [35]; in which Co$^{2+}$ ions existing mostly in the tetra-coordination state showed a shielding behavior towards the effects of progressive gamma irradiation especially in the visible spectral region. The evolution of structure, phase composition and spectroscopic properties of CoO-doped titania-containing zinc aluminosilicate glasses with their heat-treatment has been studied using Raman scattering, small angle X-ray scattering, X-ray diffraction analysis and optical absorption spectra by Alekseeva et al [36].
The review clearly indicates virtually no devoted studies on structural probing of cobalt ions in lead bismuth arsenate glasses are available.

5.3 Results

5.3.1 Physical parameters

From the measured values of density \( d \) and calculated average molecular weight \( \overline{M} \), various physical parameters such as cobalt ion concentration \( N_i \) and mean cobalt ion separation \( r_i \) of these glasses are evaluated using the conventional formulae and are presented in Table 5.1.

<table>
<thead>
<tr>
<th>Glass sample</th>
<th>Density (g/cm(^3))</th>
<th>Conc. ( \text{Co}^{2+} ) ions, ( N_i ) ((10^{19}/\text{cm}^3))</th>
<th>Inter ionic distance ( R_i ) (nm)</th>
<th>Polaron radius ( R_p ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(_1)</td>
<td>6.812</td>
<td>1.65</td>
<td>8.456</td>
<td>3.407</td>
</tr>
<tr>
<td>Co(_2)</td>
<td>6.809</td>
<td>3.31</td>
<td>6.711</td>
<td>2.704</td>
</tr>
<tr>
<td>Co(_3)</td>
<td>6.806</td>
<td>4.96</td>
<td>5.862</td>
<td>2.362</td>
</tr>
<tr>
<td>Co(_4)</td>
<td>6.803</td>
<td>6.62</td>
<td>5.326</td>
<td>2.146</td>
</tr>
<tr>
<td>Co(_5)</td>
<td>6.800</td>
<td>8.28</td>
<td>4.944</td>
<td>1.992</td>
</tr>
<tr>
<td>Co(_6)</td>
<td>6.797</td>
<td>9.93</td>
<td>4.652</td>
<td>1.874</td>
</tr>
</tbody>
</table>

5.3.2 Differential thermal analysis (DTA)

Differential thermal analysis (DTA) of the glass samples is carried out in the temperature region 30–1000 °C. DTA pattern for one of the glass samples viz., Co\(_4\) is shown in Fig. 5.1. From the traces of DTA, the glass
stability factors against devitrification viz., \((T_c - T_g)\) and the Hruby’s parameter \((K_{gl} = (T_c - T_g) / (T_m - T_c))\) are evaluated and presented in Table 5.2. The parameters indicated the highest thermal stability against devitrification for PbO–Bi\(_2\)O\(_3\)–As\(_2\)O\(_3\) glass system when the concentration of the dopant (CoO) is 0.4 mol % (inset of Fig. 5.1).

Fig. 5.1 DTA trace of Co\(_4\) glass sample. Inset shows the variation of Hruby parameter \((K_{gl})\) with the concentration of CoO.
Table 5.2
Data on differential thermal analysis (DTA) of PbO–Bi₂O₃–As₂O₃: CoO glass system.

<table>
<thead>
<tr>
<th>Glass sample</th>
<th>T_g (°C)</th>
<th>T_c (°C)</th>
<th>T_m (°C)</th>
<th>(T_c – T_g)</th>
<th>K_gl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₁</td>
<td>303</td>
<td>521</td>
<td>836</td>
<td>218</td>
<td>0.692</td>
</tr>
<tr>
<td>Co₂</td>
<td>316</td>
<td>538</td>
<td>829</td>
<td>222</td>
<td>0.763</td>
</tr>
<tr>
<td>Co₃</td>
<td>322</td>
<td>548</td>
<td>819</td>
<td>226</td>
<td>0.834</td>
</tr>
<tr>
<td>Co₄</td>
<td>329</td>
<td>556</td>
<td>815</td>
<td>227</td>
<td>0.877</td>
</tr>
<tr>
<td>Co₅</td>
<td>305</td>
<td>526</td>
<td>831</td>
<td>221</td>
<td>0.725</td>
</tr>
<tr>
<td>Co₆</td>
<td>301</td>
<td>518</td>
<td>841</td>
<td>217</td>
<td>0.672</td>
</tr>
</tbody>
</table>

5.3.3 Dielectrical properties

The temperature dependence of $\varepsilon'$ of the glasses containing different concentrations of CoO at 1 kHz is shown in Fig. 5.2 and at different frequencies of glass Co₅ is shown as the inset. The value of $\varepsilon'$ is found to exhibit a considerable increase at higher temperatures especially at lower frequencies; the rate of increase of $\varepsilon'$ with temperature is found to be the lowest for the glass containing 0.4 mol% of CoO.

A comparison plot of variation of $\tan\delta$ with temperature, measured at a frequency of 10 kHz is presented in Fig. 5.3 and the temperature dependence of $\tan\delta$ of for one of the glasses (glass Co₁) at different frequencies is shown as an inset of the same figure. The curves of CoO doped glasses have exhibited
Fig. 5.2 A comparison plot of variation of dielectric constant with temperature at 1 kHz for PbO-Bi₂O₃-As₂O₃: CoO glasses. Inset gives the variation of dielectric constant with temperature at different frequencies of glass Co₅.

Distinct maxima; with increasing frequency, the temperature maximum shifts towards higher temperature and with increasing temperature the frequency maximum shifts towards higher frequency, indicating the dielectric relaxation
Fig. 5.3 A comparison plot of variation of dielectric loss with temperature at 10 kHz for PbO-Bi$_2$O$_3$-As$_2$O$_3$: CoO glasses. Inset gives the variation of tan $\delta$ with temperature at different frequencies of glass Co$_1$. 
character of dielectric losses of these glasses. Further, the observations on
dielectric loss variation with temperature with different concentrations of CoO
(up to 0.4 mol %) indicated a decrease in the broadness and (\(\tan \delta\))\text{max} of
relaxation curves. From these curves, the effective activation energy \(W_d\), for
the dipoles is evaluated for different concentrations of CoO; the activation
energy is found to be the highest for the glass Co\(_4\) and the lowest for glass Co\(_6\)
(Table 5.3).

Table 5.3

Data on dielectric properties of PbO–Bi\(_2\)O\(_3\)–As\(_2\)O\(_3\): CoO glasses.

<table>
<thead>
<tr>
<th>Glass sample</th>
<th>A.E for dipoles(eV)</th>
<th>A.E for conduction(eV)</th>
<th>Spreading factor (\beta) (radian)</th>
<th>(N(E_F)\times10^{20}) (eV(^{-1})/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(_1)</td>
<td>1.86</td>
<td>0.47</td>
<td>0.59</td>
<td>4.85</td>
</tr>
<tr>
<td>Co(_2)</td>
<td>2.01</td>
<td>0.57</td>
<td>0.49</td>
<td>3.66</td>
</tr>
<tr>
<td>Co(_3)</td>
<td>2.27</td>
<td>0.61</td>
<td>0.42</td>
<td>2.74</td>
</tr>
<tr>
<td>Co(_4)</td>
<td>2.73</td>
<td>0.89</td>
<td>0.39</td>
<td>2.35</td>
</tr>
<tr>
<td>Co(_5)</td>
<td>1.92</td>
<td>0.51</td>
<td>0.51</td>
<td>4.38</td>
</tr>
<tr>
<td>Co(_6)</td>
<td>1.84</td>
<td>0.42</td>
<td>0.63</td>
<td>4.89</td>
</tr>
</tbody>
</table>
The a.c. conductivity $\sigma_{ac}$ is calculated at different temperatures for different frequencies and the plot of log $\sigma_{ac}$ against $1/T$ for all the glasses at 100 kHz (Fig. 5.4) and for one of the glasses viz., Co$_3$ at different frequencies is shown as the inset (a) of the same figure; the conductivity is found to decrease considerably with increase in the concentration of CoO at any given frequency and temperature up to 0.4 mol% of CoO. From these plots, the activation energy for the 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 presented in Table 5.3. The activation energy is found to decrease with increase of CoO content beyond 0.4 mol%.

The IR spectra (Fig. 5.5) of the studied glass samples have exhibited only two bands corresponding to Bi-O vibrations of BiO$_6$ and BiO$_3$ units at 470 cm$^{-1}$ and 840 cm$^{-1}$ respectively [37]. Additionally, the spectra have exhibited the fundamental bands of As$_2$O$_3$ units [38] corresponding to $\nu_1$ (1050 cm$^{-1}$), $\nu_2$ (620 cm$^{-1}$) and $\nu_3$ (750 cm$^{-1}$) vibrations. In the region of symmetrical bending vibrations of BiO$_6$ units a band due to vibrations of PbO$_4$ structural units is also predicted as mentioned earlier [39-41]. Hence presence of Bi–O–Pb linkages is also possible in the glass network. In the spectra of the samples containing higher concentrations of CoO (Co$_5$ and Co$_6$) a weak band assigned to Co$^{III}$–O vibrations is also detected [42]. As the concentration of CoO is increased upto
0.4 mol%, the intensity of symmetrical stretching vibrations of As$_2$O$_3$ units and BiO$_3$ structural units is observed to increase. When the concentration of CoO is raised beyond 0.4 mol%, the intensity of the band due to BiO$_6$ structural units raised beyond 0.4 mol%, the intensity of the band due to BiO$_6$ structural units

![Graph](image)

**Fig. 5.4** Variation of sac with 1/T at 100 kHz of PbO-Bi$_2$O$_3$-As$_2$O$_3$: CoO glasses. Inset (a) represents the variation of a.c. conductivity with temperature at different frequencies of glass Co$_3$. Inset (b) Variation of conductivity at 100 kHz and 280 °C with the activation energy for conduction.
Fig. 5.5 IR spectra of PbO-Bi$_2$O$_3$-As$_2$O$_3$: CoO glasses.
is found to prevail over that of BiO$_3$ structural units. The summary of the IR band positions due to different functional groups of PbO–Bi$_2$O$_3$–As$_2$O$_3$ is presented in Table 5.4.

**Table 5.4** Data on infrared spectra of PbO–Bi$_2$O$_3$–As$_2$O$_3$: CoO glasses recorded at room temperature (Assignment of band positions in cm$^{-1}$).

<table>
<thead>
<tr>
<th>Glass sample</th>
<th>PbO$_4$/Bi–O vibration of [BiO$_6$]</th>
<th>Co$^{III}$–O vibration</th>
<th>$\nu_2$-As$_2$O$_3$</th>
<th>$\nu_3$-As$_2$O$_3$</th>
<th>Bi–O stretching vibrations of BiO$_3$</th>
<th>$\nu_1$-As$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_1$</td>
<td>474</td>
<td>-</td>
<td>624</td>
<td>759</td>
<td>850</td>
<td>1068</td>
</tr>
<tr>
<td>Co$_2$</td>
<td>470</td>
<td>-</td>
<td>618</td>
<td>754</td>
<td>848</td>
<td>1065</td>
</tr>
<tr>
<td>Co$_3$</td>
<td>471</td>
<td>-</td>
<td>612</td>
<td>756</td>
<td>845</td>
<td>1063</td>
</tr>
<tr>
<td>Co$_4$</td>
<td>469</td>
<td>-</td>
<td>610</td>
<td>746</td>
<td>841</td>
<td>1061</td>
</tr>
<tr>
<td>Co$_5$</td>
<td>469</td>
<td>567</td>
<td>620</td>
<td>757</td>
<td>849</td>
<td>1066</td>
</tr>
<tr>
<td>Co$_6$</td>
<td>469</td>
<td>571</td>
<td>622</td>
<td>762</td>
<td>852</td>
<td>1069</td>
</tr>
</tbody>
</table>

Fig. 5.6 presents the optical absorption spectra of PbO–Bi$_2$O$_3$–As$_2$O$_3$: CoO glass samples recorded at room temperature in the spectral wavelength region 300-2000 nm. The absorption edge observed at 389 nm for the glass sample Co$_1$ is found to be spectrally shifted towards lower wavelength with increase in the concentration of CoO up to 0.4 mol%. From the observed absorption edges, we have evaluated the optical band gaps ($E_o$) of these samples by drawing Tauc plots (Fig. 5.7) between ($\alpha h\omega$)$^{1/2}$ and $h\omega$. The values of optical band gap ($E_o$) is determined and are presented in Table 5.5. The value of $E_o$, is observed to
increase with increase in the concentration of CoO up to 0.4 mol% beyond that a reversal trend is observed.

Fig. 5.6 Optical absorption spectra of PbO-Bi2O3-As2O3:CoO glasses

Fig. 5.7 Evaluation of the optical band gap for PbO–Bi2O3–As2O3: CoO glass samples
The spectrum of CoO free glass exhibited two significant kinks due to $^{3}P_0 \rightarrow ^{1}S_0$ (at about 510 nm) and $^{3}P_0 \rightarrow ^{1}D_2$ (715 nm) transitions of Bi$^{3+}$ ions [43].

Table 5.5
Summary of the data on optical absorption spectra of PbO–Bi$_2$O$_3$–As$_2$O$_3$: CoO glass system.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Optical band gap $E_o$ (eV)</th>
<th>$^{3}P_0 \rightarrow ^{1}S_0$ (Bi$^{3+}$ ions)/$^{4}T_{1g}(F) \rightarrow ^{2}T_{1g}(H)$ (O$_h$) Co$^{2+}$ ions</th>
<th>$^{4}A_2(^4F) \rightarrow ^{4}T_{1g}(^4P)$ (T$_d$) Co$^{2+}$ ions</th>
<th>$^{3}P_0 \rightarrow ^{1}D_2$ (Bi$^{3+}$ ions) / $^{2}E \rightarrow ^{2}T_2$ (O$_h$) Co$^{3+}$ ions</th>
<th>$^{4}A_2(^4F) \rightarrow ^{4}T_1(^4F)$ (T$_d$) Co$^{3+}$ ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_1$</td>
<td>2.68</td>
<td>494</td>
<td>575</td>
<td>704</td>
<td>1443</td>
</tr>
<tr>
<td>Co$_2$</td>
<td>2.76</td>
<td>502</td>
<td>582</td>
<td>699</td>
<td>1452</td>
</tr>
<tr>
<td>Co$_3$</td>
<td>2.91</td>
<td>504</td>
<td>589</td>
<td>689</td>
<td>1464</td>
</tr>
<tr>
<td>Co$_4$</td>
<td>2.98</td>
<td>507</td>
<td>593</td>
<td>685</td>
<td>1481</td>
</tr>
<tr>
<td>Co$_5$</td>
<td>2.72</td>
<td>498</td>
<td>583</td>
<td>701</td>
<td>1448</td>
</tr>
<tr>
<td>Co$_6$</td>
<td>2.63</td>
<td>491</td>
<td>570</td>
<td>707</td>
<td>1431</td>
</tr>
</tbody>
</table>

The spectrum of the sample Co$_1$ exhibited two additional bands at 570 nm due to $^{4}A_2(^4F) \rightarrow ^{4}T_1(^4P)$ and 1470 nm $^{4}A_2(^4F) \rightarrow ^{4}T_1(^4F)$ tetrahedral transitions of Co$^{2+}$ ions. In the region of $^{3}P_0 \rightarrow ^{1}S_0$ transition of Bi$^{3+}$ ions and octahedral band due to $^{4}T_{1g}(F) \rightarrow ^{2}T_{1g}(H)$ transition of Co$^{2+}$ ions is predicted. Similarly, in the spectral region of $^{3}P_0 \rightarrow ^{1}D_2$ transitions of Bi$^{3+}$ ions an octahedral excitation band of ($^{2}E \rightarrow ^{2}T_2$) Co$^{3+}$ ions is also possible [44, 45]. As the concentration of CoO increased up to 0.4 mol% a gradual increase of tetrahedral band intensities is observed. When the concentration of CoO is raised beyond 0.4 mol%, the octahedral bands are observed to grow at the expense of tetrahedral bands. The
summary of various absorption band positions of cobalt ions in PbO–Bi$_2$O$_3$–As$_2$O$_3$ glasses is presented in Table 5.5.

5.4 Discussion

In PbO–Bi$_2$O$_3$–As$_2$O$_3$ glass matrix, the cobalt ions are expected to exist in two viable valance states: i) primarily, Co$^{2+}$ which occupy both the tetrahedral and octahedral coordination with oxygen ions and also in ii) Co$^{3+}$ state with octahedral occupancy. The energy level structure of the Co$^{2+}$(d$^7$) ion in tetrahedral site is similar to the energy level structure of d$^3$ ions in octahedral site.

The observed trends of intensity of various optical absorption bands indicate that as the concentration of CoO is raised beyond 0.4 mol% in the glass system there is a gradual transformation of Co$^{2+}$ ions from tetrahedral occupancy to octahedral occupancy. The octahedrally coordinated Co$^{2+}$ ions and even Co$^{3+}$ ions act as modifiers similar to Pb$^{2+}$ ions and induce non-bridging oxygens (NBOs) in the glass network where as the tetrahedral cobalt ions participate in the glass network with the cross linkages of the other constituents of glass network. Lower is the concentration of the modifier (octahedral ions) ions, the lower is the concentration of NBO’s in the glass matrix. Because of this reason, a decrease in the degree of localization of electrons there by a decrease in the donor centers in the glass network is anticipated. The presence of smaller concentration of these donor centers
increases the optical band gap and shifts the absorption edge towards lower wavelength side as observed when the concentration of CoO is increased up to 0.4 mol% (Fig. 5.8). The gradual increase in the proportion of network forming Co\(^{2+}\) ions in the glass network results a decrease the generation of donor centers; as a consequence, there will be a decreasing overlap between empty 3d states of Co\(^{2+}\) sites and the neighbouring excited states of localized electrons originally trapped on Co\(^{3+}\) ions. Such separation leads to the enlargement of optical band gap as observed for the sample Co\(_1\) to Co\(_4\) (Table 5.3).

In the IR spectra, with gradual increase in the concentration of CoO up to 0.4 mol %, the intensity of BiO\(_3\) structural units is observed to increase. Tetragonally positioned Co\(^{2+}\) ions do not induce any dangling bands but octahedral positioned Co\(^{2+}\) ions may do so [46]. The increase in the intensity of the band due to BiO\(_6\) structural units at the expense of the band due to BiO\(_3\) structural units when the concentration of CoO is raised beyond 0.4 mol% suggests the decrease in the concentration of tetrahedral cobalt ions the glass network.

The considerable increase of dielectric constant \(\varepsilon'\) with temperature of the studied glasses can be attributed to space-charge polarization due to bonding defects produced by the modifiers [47]. With the addition of the dopant (CoO) concentration beyond 0.4 mol % to PbO–Bi\(_2\)O\(_3–\)As\(_2\)O\(_3\) glass
system, the rate of increase of $\varepsilon'$ with temperature is gradually increased; indicating a growing degree of disorder that contributes to the space-charge polarization. The basis for this argument can be cited from the results of optical absorption, IR and DTA studies which have indicated that the cobalt ions mostly exist in octahedral coordination in this concentration range. These ions act as modifiers and generate bonding defects by breaking Bi–O–Pb, Bi–O–Bi, As–O–Bi bonds and contribute for the increase in the dielectric parameters as observed [48, 49]. When the concentration of the CoO is intermediate ($x= 0.4$ mol%) in the glass system, as stated earlier, a considerable proportion of cobalt ions do exist in tetrahedrally coordinated $\text{Co}^{2+}$ state in addition to the octahedrally coordinated $\text{Co}^{2+}$ state and $\text{Co}^{3+}$ state; these ions take network forming positions, increase the rigidity of the glass network resulting to decrease of dielectric parameters as observed.

Among different constituents of these glasses, the octahedral divalent cobalt ions together with a pair of cationic vacancies may form dipoles and such types of dipoles are responsible for the observed dielectric relaxation effects [50, 51]. Additionally there are also reports suggesting that $\text{Bi}^{3+}$ ions do contribute to the dielectric relaxation effects [52]. The shifting of relaxation region towards lower temperatures (Fig. 5.3) and decrease in the activation energy for the dipoles with the increase the concentration of CoO beyond 0.4 mol% (Table 5.3) suggests an increasing degree of freedom for dipoles to
orient in the field direction in the glass network. The lowest relaxation intensity observed for the glass Co$_4$ supports the earlier argument that a considerably larger concentration of Co$^{2+}$ ions takes network forming positions with tetrahedral coordination in the glass network.

Conventionally, the dielectric relaxation effects are described with the variable frequency at a fixed temperature. However, similar information can also be obtained by analyzing these results at a fixed frequency at variable temperature as suggested by Bottcher and Bordewijk [53].

Substituting conventional equation viz.,

$$\tau = \tau_0 e^{E_a/k_BT}$$

(5.1)

in standard Debye relations for dielectric relaxation, viz.,

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2}$$

(5.2)

$$\varepsilon''(\omega) = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + \omega^2 \tau^2}$$

(5.3)

one can obtain

$$\varepsilon'(\omega,T) = \varepsilon_\infty + \frac{1}{2}(\varepsilon_s - \varepsilon_\infty)[1 - tgh(E_a/kT + \ln\omega\tau)]$$

(5.4)

$$\varepsilon''(\omega,T) = \frac{\frac{1}{2}(\varepsilon_s - \varepsilon_\infty)}{\cosh(E_a/kT + \ln\omega\tau)}$$

(5.5)

In Eqs. (5.4) and (5.5), $\varepsilon_\infty$ is temperature independent whereas $\varepsilon_s$ is largely dependent on temperature. Keeping in mind, the variation of hyperbolic
trigonometric functions in eqns. (5.4) and (5.5) with temperature is very minute, these Eqs. can be rewritten as

$$
\varepsilon' (\omega, T) = \varepsilon_\infty + \frac{1}{2} (\varepsilon_s - \varepsilon_\infty) \left[ 1 - \tgh \left( \frac{E_s (1/T - 1/T_m (\omega))}{k} \right) \right] \tag{5.6}
$$

and

$$
\varepsilon'' (\omega, T) = \frac{1}{2} \varepsilon_\infty \cosh \left( \frac{E_s (1/T - 1/T_m (\omega))}{k} \right) \tag{5.7}
$$

In these Eqs. (5.6) and (5.7), $T_m (\omega)$ is the temperature at where $\varepsilon'$ exhibits maximum value. Thus, as per the Eqs. (5.6) and (5.7), the plots of $\varepsilon'(\omega, T)$ and $\varepsilon'' (\omega, T)$ against $1/T$ should be centro symmetric and symmetric curves respectively in the dielectric relaxation region. As an example for one of the glass samples (viz., Co$_4$) under investigation, the variation of $\varepsilon'(\omega, T)$ and $\varepsilon'' (\omega, T)$ with $1/T$ are shown in Fig. 5.8.

The shape of these curves is well in accordance with the Eqs. (5.6) and (5.7) and clearly confirms the relaxation character of dielectric properties of these glasses. The nature of variation of $\varepsilon'(T)$ and $\tan \delta$ with temperature for these glasses indicates that the Cole-Davidson equation:

$$
\varepsilon^* (\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + i\omega \tau)^{1/\beta}} \tag{5.8}
$$

can safely be applied to these glasses. Separating real and imaginary terms of Eq. (5.8), and rewriting with explicit temperature dependence of terms:
Fig. 5.8 Variation of $\varepsilon'(\omega, T)$ and $\varepsilon''(\omega, T)$ with $1/T$ for glass Co$_4$.

\[ \varepsilon'(\omega, T) = \varepsilon_\infty + (\varepsilon_1 - \varepsilon_\infty)[\cos \phi(T)]^\beta \cos \beta \phi(T) \] (5.9)
\[ \varepsilon'(\omega, T) = (\varepsilon_s - \varepsilon_\infty) \left[ \cos \varphi(T) \right]^\beta \sin \beta \varphi(T). \] \hspace{1cm} (5.10)

Where, \( \varphi(T) = \tan^{-1}(\omega \tau) = \tan^{-1}(\omega A_0 e^{W_d/KA_T}) \) \hspace{1cm} (5.11)

In Eq. (5.11) \( A_0 \) is a constant and \( W_d \) is the activation energy. The plot between \( \varepsilon'(T) \) and \( \varepsilon''(T) \) given by the Eqs. (5.9) and (5.11) at a fixed frequency is often called a pseudo Cole-Cole plot, which cuts \( \varepsilon' \) axis at \( \varepsilon_s \) and \( \varepsilon_\infty \). Here, \( \varepsilon_s \) is known as high temperature dielectric constant (in contrast to the low frequency dielectric constant in the conventional Cole-Cole plot) and similarly \( \varepsilon_\infty \) is the low temperature dielectric constant. The plot cuts \( \varepsilon' \) axis at an angle of \( (\pi/2) \beta \) at low temperature side (as per Sixou [54]), here \( \beta \) is the spreading factor for relaxation times. For PbO-Bi\(_2\)O\(_3\)-As\(_2\)O\(_3\) glass doped with 0.5 % of CoO, a pseudo Cole-Cole plot at 100 kHz is shown in Fig. 5.10. The spreading factor \( \beta \) estimated from this plot is 0.51 radians; such plots have also been drawn for all the glasses and the value of \( \beta \) is estimated in a similar way. The value of \( \beta \) is found to decrease gradually with the concentration of CoO up to 0.4 mol% (Table 5.3). Thus the analysis indicates that there is a spreading of relaxation times. The spreading of relaxation times suggests that there are multiple types of dipoles are present in the glass system.
When a plot is made between log $\sigma(\omega)$ vs activation energy for conduction (in the high temperature region) a near linear relationship is observed (inset (b) of Fig. 5.4); this observation suggests that the conductivity enhancement is directly related to the thermally stimulated mobility of the charge carriers in the high temperature region.

The conductivity isotherm shown in Fig. 5.10 as a function of the concentration of CoO passes through a minimum at $x = 0.4$ mol %. Though electronic and ionic conductivities are not separated but the observed trend of decrease of conductivity and increase of activation energy for $x < 0.4$ mol% (zone-1) and, increase of conductivity and decrease of activation energy for $x >$
0.4 mol% of CoO content (zone-2), suggests switch over of predominance of conduction mechanism from electronic to ionic [56]. The mobile electrons, or polarons, involved in the process of transfer from $\text{Co}^{2+} \leftrightarrow \text{Co}^{3+}$, are attracted by the oppositely charged cations. This cation-polaron pair moves together as a neutral entity. As expected, the migration of this pair is not associated with any net displacement of the charge and thus does not contribute to electrical conductivity. As a result, we expect a decrease in the conductivity, as observed in zone-1. In other words, when the concentration of CoO is less than 0.4 mol%, the associated electrons with the copper ions are trapped at deeper sites within the main band gap and have larger wave-function radii. This kind of mechanism is possible due to the fact that the local potential fluctuation is small as compared to the hopping rate. The situation will however be reversed if the concentration of CoO is greater than 0.4 mol% due to larger degree of disorder in the glass network.

The a.c conductivity in the low temperature region (where the conductivity is nearly temperature independent) can be understood based on quantum mechanical tunneling model. Based on Austin and Mott’s model (quantum mechanical tunneling model) [57], the density of the energy states near the Fermi level, $\text{N}(E_F)$, at nearly temperature independent region of the conductivity (low temperature) is evaluated as per the procedure mentioned in Chapter 3.
The value of \( N(E_F) \) is found to decrease gradually from the sample Co\(_1\) to Co\(_4\), indicating a decreasing degree of disorder with increase in the content of CoO in the glass network in this concentration range.

Our observations on dielectric parameters of PbO–Bi\(_2\)O\(_3\)–As\(_2\)O\(_3\): CoO glasses, as mentioned earlier, indicate the rate of increase of \( \epsilon \tan \delta \) (which is inversely proportional to breakdown strength) with temperature is the highest for the glass Co\(_6\) and the lowest for the glass Co\(_4\). Thus the studies on dielectric properties of these glasses also reveal that there is an increase in the dielectric breakdown strength of the glasses with increase in the concentration of CoO up
to 0.4 mol %. These revelations are also consistent with the view that, in the concentration range of 0.1 to 0.4 mol %, the cobalt ions prevailingly occupy network forming positions with the gradual reduction of cobalt ions from octahedral sites to tetrahedral sites and increase the insulating strength of the glass samples.

### 5.5 Conclusions

The glasses of the composition viz., (40-x) PbO–15 Bi₂O₃–45As₂O₃–x CoO, with 0 ≤ x ≤ 0.6 mol% in the steps of 0.1 were synthesized. Dielectric and spectroscopic properties were investigated. The optical absorption spectra reveal a small concentration of cobalt ions do exists in Co³⁺ state with octahedral coordination, in addition to tetrahedral and octahedral Co²⁺ ions. The tetrahedral occupancy of Co²⁺ ions prevails over octahedral occupancy in the samples containing CoO from 0.1 to 0.4 mol%. The IR spectral results indicated the degree of disorder in the glass network is more in the glasses containing CoO greater than 0.4 mol%. The studies on dielectric properties of these glasses revealed that there is an increase in the insulating strength of the glasses with increase in the concentration of CoO up to 0.4 mol %.
References


