Structural and Electrical properties of ZnF$_2$-Bi$_2$O$_3$-GeO$_2$ glasses doped with CoO

5.1 Introduction:

Germanate glasses mixed with heavy metal oxides are known to be promising materials for IR technological applications such as non-linear optical fibers and laser devices as reported by Marcel [1]. In view of its properties like high refractive index, high dispersion and transmission in the IR region, such glass matrices are used as specialty glasses, in particular as light guiding core of an optical fibre glasses transmitting IR radiation [2, 3]. They are stable against devitrification and moisture resistance [4]. GeO$_2$ is a typical glass former [5] and germanate glasses are being used as IR transmitting windows [6].

Bi$_2$O$_3$ participate in the glass structure with two coordinations as network former in the form of BiO$_3$ (pyramidal) and as network modifier such as BiO$_6$ (octahedral) units [7-8]. Bismuth ion was reported as an efficient luminescent activator [9]. Fluoride glasses typically have infrared absorption edge wavelengths in the range 6 to 8 µm. With the addition of ZnF$_2$ (metal fluoride) to heavy metal germanate glasses widen their transmitting range into the infrared [10]. The glasses containing cobalt ions are useful for nonlinear optical absorbers, needed for passive modulations of laser beams. These materials are also considered as useful materials for
Q-switching devices [11-14]. Moreover CoO influence the electrical properties of the host glass to the considerable level. In the glass matrix cobalt ions exist in two stable states Co$^{2+}$ and/or Co$^{3+}$. Co$^{2+}$ ions create color centers (blue and pink) with absorption band in the visible and NIR region [15], the intensity of such colour centres increases with an increase in the Co$^{2+}$ ion concentration.

Photo luminescence studies such as infrared to visible up conversion of Er$^{3+}$ with glass compositions GeO$_2$-PbO-Nb$_2$O$_5$; GeO$_2$-PbO-CaCO$_3$; GeO$_2$-PbO-BaO-ZnO-K$_2$O; GeO$_2$-PbO-CaO-TeO$_2$; GeO$_2$-Bi$_2$O$_3$ and GeO$_2$-PbO-Bi$_2$O$_3$ [16-19]. NIR properties of GeO$_2$-PbO-Bi$_2$O$_3$ glasses doped with Yb$^{3+}$ ions are reported by Kassab et al [20]. Salem and Mohammad reported the electrical studies such as d.c., a.c. conductivities and other dielectric properties of Bi$_2$O$_3$-GeO$_2$-MoO$_3$ glasses, in which the molybdenum ions hindered the electron motion in the glass matrices [21]. Durga et. al., [22] studied dielectric dispersion in ZnF$_2$-Bi$_2$O$_3$-TeO$_2$ glass system. Recently Srinivasaraao et al. [23] have reported structural properties of ZnF$_2$-Bi$_2$O$_3$-P$_2$O$_5$ glass system by means of spectroscopic and dielectric studies from our laboratory.

In view of the above potential applications besides moderate work such as structural properties via dielectric and spectroscopic studies reported only on bismuth – germinate glass system. Further the addition of
zinc fluoride and cobalt oxide doping to the bismuth-germanate glass improves the mechanical strength, chemical durability and conductivity of the glass matrix. Therefore the authors have chosen the present glass composition 20ZnF$_2$ - 40Bi$_2$O$_3$ - (40-x)GeO$_2$: xCoO; 0 ≤ x ≤ 1.0 in order to investigate the spectroscopic properties (viz., FTIR, Raman, optical absorption) along with dielectric studies (dielectric constant $\varepsilon'$, loss (tan$\delta$), ac conductivity $\sigma_{ac}$) over a wide range of frequency and moderate temperature region.

In the present investigation, glass samples with composition 20ZnF$_2$ - 40Bi$_2$O$_3$ - (40-x)GeO$_2$: xCoO ; 0 ≤ x ≤ 1.0 wt% (ZBiG:Co) are prepared using melt-quenching method. The prepared samples are labelled as

$C_0$: 20ZnF$_2$-40Bi$_2$O$_3$- 40GeO$_2$

$C_1$: 20ZnF$_2$-40Bi$_2$O$_3$- 39.8GeO$_2$: 0.2CoO

$C_2$: 20ZnF$_2$-40Bi$_2$O$_3$ - 39.6GeO$_2$: 0.4CoO

$C_3$: 20ZnF$_2$-40Bi$_2$O$_3$- 39.4GeO$_2$: 0.6CoO

$C_4$: 20ZnF$_2$-40Bi$_2$O$_3$- 39.2GeO$_2$: 0.8CoO

$C_5$: 20ZnF$_2$-40Bi$_2$O$_3$- 39GeO$_2$: 1.0CoO (all are in wt%)

Analytical grade reagents of GeO$_2$, Bi$_2$O$_3$, ZnF$_2$ and CoO (Sigma Aldrich 99.99% pure) are thoroughly mixed in an agate mortar and melted
in a silica crucible at 1050 °C for 20 minutes until a bubble free liquid is formed. The melt is then poured in a brass mould and subsequently annealed at 400 °C. Transparent yellow (pure) and blue (doped) glasses are obtained and the color of prepared glasses increases with increasing dopant concentration.

Fig. 5.1 shows the physical appearance of the glasses in the present investigation.

![Fig. 5.1 Physical appearance of the glasses](image)

Fig. 5.1 Physical appearance of the 20ZnF$_2$-40Bi$_2$O$_3$- (40-x)GeO$_2$: xCoO glasses

5.2. Brief review of the previous work on the on CoO doped glasses

Volk et al. [24] studied on stimulated emission of Co$^{2+}$-doped glass–ceramics. The materials studied are lithium-, magnesium-, magnesium – zinc-, and magnesium – gallium – aluminosilicate glass – ceramics doped with 0.05 – 0.1 wt% CoO. The stimulated-emission band in the 620 – 700 nm region is observed in all glass–ceramic materials and is assigned to the
$^{4}T_{1}(^{4}P) \rightarrow ^{4}A_{2}$ transition of tetrahedrally coordinated divalent cobalt ion. Optical characterization of Mn$^{2+}$, Ni$^{2+}$ and Co$^{2+}$ ions doped zinc lead borate glasses were reported by Thulasiramudu and Buddhudu [25] In these studies they found through various optical tools suggest that these glasses have potential applications as luminescent optical materials. Optical properties of Co$^{2+}$-doped Li$_{2}$O–Ga$_{2}$O$_{3}$–SiO$_{2}$ glass-ceramics were studied by Xiulan Duan et al. [26] the samples crystallized to LiGa$_{5}$O$_{8}$ nanocrystals with the size of 6 nm and exhibited a broad absorption band near 1500 nm, which is characteristic of tetrahedral Co$^{2+}$ ions in crystals. The emission in the visible and near infrared (NIR) region was observed from the glass ceramics and attributed to the $^{4}T_{1}(^{4}P) \rightarrow ^{4}A_{2}(^{4}F)$ and $^{4}T_{1}(^{4}P) \rightarrow ^{4}T_{2}(^{4}F)$ transitions of tetrahedral Co$^{2+}$, respectively. Raghavendra Rao et al. [27] studied the correlation between physical and structural properties of Co$^{2+}$ doped mixed alkali zinc borate glasses by means of XRD, FTIR and optical absorption. Optical absorption spectra also confirm the near octahedral site symmetry for Co$^{2+}$ ions with partial covalency of ZLN or glasses. The non-linear behavior is observed in crystal field parameter D$_{q}$ which indicates the minimum structural distortion at $x = 15$ mol%. Site symmetry of Mn(II) and Co(II) in zinc phosphate glass were studied through optical absorption and EPR spectra of Mn(II) and Co(II) doped zinc phosphate glasses have been investigated by Ravikumar et al. [28]. From the results and analysis of the
optical absorption and EPR spectra of the Mn(II) and Co(II) doped zinc phosphate glasses, octahedral coordination for the ions is suggested. By correlating optical and EPR data, bonding parameters are evaluated. They suggest predominantly ionic nature for the bonding between the TM ions and host glass ions. Sankarappa et al. [29] studied the a. c. conductivity and dielectric studies in V₂O₅–TeO₂– and V₂O₅–CoO–TeO₂ glasses. In these studies they found that temperature dependence of ac conductivity at different frequencies and dc conductivity exhibit the behaviour at high temperatures similar to that predicted by the Mott’s small polaron hopping model. The ac conductivity appeared to be behaving as per the Hunt’s expression given for ω > ωₘ where ωₘ (=F₀) correspond to dielectric peak. Structural investigations of PbO – Sb₂O₃ – B₂O₃:CoO glass ceramics were studied by Satyanarayana et al. [30] using spectroscopic and dielectric studies. The study of DSC suggests that, crystallization spreads from the inside to the surface of the samples as the concentration of CoO is increased. These studies together with the result of magnetic susceptibility experiments have indicated that, with the increase in the concentration of the nucleating agent there is a gradual transformation of cobalt ions from tetragonal to octahedral coordination. Structural changes in CoO doped PbO - As₂O₃ glass ceramics were reported by Nagarjuna et al. [31]. Optical absorption, IR and photoluminescence studies of these samples have been
carried out. The analysis of the results of these studies has indicated that the cobalt ions exist in Co$^{2+}$ and Co$^{3+}$ states in the glass matrix. The studies revealed that as the concentration of the CoO is increased, there is a gradual transformation of cobalt ions from tetrahedral to octahedral positions. Optical and thermal properties of $\text{P}_2\text{O}_5$–$\text{Na}_2\text{O}$–$\text{CaO}$–$\text{Al}_2\text{O}_3$:CoO glasses were reported by Colak and Aral [32]. The incorporation of CoO at 20% almost destroys absorption in the visible region from the absorption spectra and doping by transition metal ions have a dramatic effect on the properties of sodium–phosphate glasses, that new and alternative glass materials may be produced economically by this process. It is also concluded that CuO doped (at 0.5%) glass is the best candidate for solar collector applications with its improved absorption characteristics and thermal conductivity values. $\text{Al}_2\text{O}_3$–$\text{SiO}_2$–$\text{TiO}_2$ glasses doped with CoO were studied by Bae et al. [33] comparing the variations in corresponding Raman scattering spectra, optical absorption spectra and X-ray diffraction patterns. At low-temperature heat-treatments ($660 – 700 \degree\text{C}$), CoO enters alumina-titanate amorphous phase, which results in increased temperature interval of existence and increased amount of this phase. Addition of CoO decreases the temperature of crystallization of the main crystalline phase, β-eucryptite solid solution. Duan et al. [34] studied spectroscopic properties of CoO: $\text{SiO}_2$–$\text{Al}_2\text{O}_3$–$\text{ZnO}$ nano-crystals. The influence of heat treatment
temperature on the luminescence spectra demonstrates the importance of energy-transfer process. The energy level structure and crystal field parameters were determined. This glass–ceramic system has potential applications as a laser material in the visible and NIR regions.

5.3. Characterization

5.3.1 X- Ray diffraction

Fig. 5.2 shows X-ray diffraction pattern of some ZBiG glasses, the

![XRD patterns of ZBiG glasses doped with CoO](image)
absence of sharp Bragg peaks confirms the amorphous nature of the prepared glasses.

### 5.3.2 Differential thermal analysis

Differential thermal analysis (DTA) thermo grams of all the samples are shown in Fig. 5.3. A typical glass transition with mid-point (average of on set and end) in the range 560-535 °C, an exothermic peak of crystallization in the range 732-694 °C and an endo-thermic peak due to melting in the range 930-925 °C of the samples are observed from the DTA spectra and the relevant data is presented in the Table 5.1.

**Fig 5.3** DTA traces of ZBiG glasses doped with CoO
The glass forming ability parameter $K_{gl}$ known as Hruby’s parameter [35] is calculated from the measured values of $T_g$, $T_c$ and $T_m$ for all the samples using the following equation and is presented in Table 5.1.

$$K_{gl} = \frac{(T_c-T_g)(T_m-T_c)}{1}$$ --- (1)

From Table 5.1, Hruby’s parameter $K_{gl}$ is found to be maximum for $C_0$ sample and it is decreased with increase in the concentration of CoO.

Table 5.1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$</th>
<th>$T_c$</th>
<th>$T_m$</th>
<th>$T_g/T_m$</th>
<th>$(T_c-T_g)/T_g$</th>
<th>$(T_c-T_g)/T_m$</th>
<th>$K_{gl}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_0$</td>
<td>560</td>
<td>732</td>
<td>930</td>
<td>0.6021</td>
<td>0.3071</td>
<td>0.1849</td>
<td>0.8686</td>
</tr>
<tr>
<td>$C_1$</td>
<td>545</td>
<td>710</td>
<td>923</td>
<td>0.5904</td>
<td>0.3027</td>
<td>0.1787</td>
<td>0.7746</td>
</tr>
<tr>
<td>$C_2$</td>
<td>542</td>
<td>706</td>
<td>921</td>
<td>0.5884</td>
<td>0.3025</td>
<td>0.1780</td>
<td>0.7627</td>
</tr>
<tr>
<td>$C_3$</td>
<td>540</td>
<td>703</td>
<td>919</td>
<td>0.5875</td>
<td>0.3018</td>
<td>0.1773</td>
<td>0.7546</td>
</tr>
<tr>
<td>$C_4$</td>
<td>538</td>
<td>699</td>
<td>918</td>
<td>0.5860</td>
<td>0.2992</td>
<td>0.1753</td>
<td>0.7351</td>
</tr>
<tr>
<td>$C_5$</td>
<td>535</td>
<td>694</td>
<td>916</td>
<td>0.5840</td>
<td>0.2971</td>
<td>0.1735</td>
<td>0.7162</td>
</tr>
</tbody>
</table>

5.3 Physical parameters

The measured density value of $C_0$ is 6.177 g/cm$^3$ and it is gradually decreased with the doping of CoO as presented in Table 5.2. In addition the
Table 5.2

Some physical parameters of ZBiG glasses doped with CoO.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Conc. of dopant x Wt%</th>
<th>Average molecular weight $\overline{M}$ (gram/mole)</th>
<th>Density $\rho$ (g/cm$^3$) (±0.001)</th>
<th>Molar Volume $V_m$ (cm$^3$/mol) (±0.001)</th>
<th>Co$^{2+}$ ion concentration $N_i \times 10^{21}$ ions/cm$^3$ (±0.01)</th>
<th>Co$^{2+}$ ion separation $R_i$ (Å) (±0.01)</th>
<th>Polaron radius $R_p$ (Å) (±0.01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_0$</td>
<td>0</td>
<td>248.91</td>
<td>6.177</td>
<td>40.29</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>C$_1$</td>
<td>0.2</td>
<td>248.85</td>
<td>6.132</td>
<td>40.58</td>
<td>2.96</td>
<td>6.95</td>
<td>2.80</td>
</tr>
<tr>
<td>C$_2$</td>
<td>0.4</td>
<td>248.79</td>
<td>6.095</td>
<td>40.81</td>
<td>5.90</td>
<td>5.53</td>
<td>2.23</td>
</tr>
<tr>
<td>C$_3$</td>
<td>0.6</td>
<td>248.73</td>
<td>6.047</td>
<td>41.13</td>
<td>8.78</td>
<td>4.84</td>
<td>1.95</td>
</tr>
<tr>
<td>C$_4$</td>
<td>0.8</td>
<td>248.68</td>
<td>6.018</td>
<td>41.31</td>
<td>11.66</td>
<td>4.30</td>
<td>1.77</td>
</tr>
<tr>
<td>C$_5$</td>
<td>1</td>
<td>248.62</td>
<td>5.972</td>
<td>41.62</td>
<td>14.46</td>
<td>4.10</td>
<td>1.65</td>
</tr>
</tbody>
</table>
molar volume is increased from $C_0$ to $C_5$. From the measured values of density \( \rho \) and calculated average molecular weight $\overline{M}$ of the glasses, some physical parameters such as mean cobalt ion concentration $N_i$, mean cobalt ion separation $R_i$, and polaron radius $R_p$ in the glass network evaluated and also presented in Table 5.2.

5.4 Results

5.4.1 Optical absorption spectra

Fig. 5.4 shows Optical absorption spectra of ZBiG glasses doped with CoO recorded at room temperature in the wavelength region 200 - 1600 nm. Pure sample $C_0$ shows two small peaks observed at 630 nm and 827 nm. The samples doped with CoO show two broad peaks in the visible region around 523 nm, 596 nm and another broad peak is observed in the NIR region at about 1434 nm. Besides these absorption bands a shoulder peak is noticed around 664 nm in all the samples. The UV absorption edge or cut off wavelength, $\lambda_c$ of $C_0$ sample is observed at 386 nm. The cut off wavelength is found to be increased from $C_0$ to $C_5$ samples.

From Tauc’s plots, drawn between $h\nu$ and $(\alpha h\nu)^{1/2}$ as shown in Fig. 5.5, optical band gap $(E_g)$ of all the samples are determined by the extrapolation of the linear portion of the curve to the x-axis $[(\alpha h\nu)^{1/2} = 0]$. The data pertinent to cut off wavelength $(\lambda_c)$, band position and band
gap($E_g$) energies for the glasses under investigation are presented in Table 5.3.

![Absorption Spectra](image)

**Fig. 5.4** Optical absorption spectra of ZBiG glass sample doped with CoO. Inset (a) shows the absorption spectrum of pure sample Co and Inset (b) shows the peak positions in the NIR region.
Table 5.3

Values of cutoff wavelength ($\lambda_c$), band position, energy band gap ($E_g$) and Urbach energy ($\Delta E$) of ZBiG glasses doped with CoO.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda_c$ (nm)</th>
<th>Position of Band</th>
<th>$E_g$ (eV) (±0.001)</th>
<th>$\Delta E$ (eV) (±0.001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Co^{2+}$ ions</td>
<td>$Co^{3+}$ ions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^4T_{1g}(F)\rightarrow^2T_{2g}(H)$</td>
<td>$^4A_2(^4F)\rightarrow^4T_{11}(^4P)$</td>
<td>$^4A_1(^4F)\rightarrow^4T_{11}(^4F)$</td>
<td>$^5T_2\rightarrow^5E$</td>
<td></td>
</tr>
<tr>
<td>(nm)</td>
<td>(nm)</td>
<td>(nm)</td>
<td>(nm)</td>
<td></td>
</tr>
<tr>
<td>$C_0$</td>
<td>386.0</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>$C_1$</td>
<td>392.0</td>
<td>523.0</td>
<td>596.0</td>
<td>1434</td>
</tr>
<tr>
<td>$C_2$</td>
<td>393.0</td>
<td>527.5</td>
<td>596.0</td>
<td>1449</td>
</tr>
<tr>
<td>$C_3$</td>
<td>394.5</td>
<td>530.0</td>
<td>597.0</td>
<td>1440</td>
</tr>
<tr>
<td>$C_4$</td>
<td>396.5</td>
<td>531.0</td>
<td>597.0</td>
<td>1425</td>
</tr>
<tr>
<td>$C_5$</td>
<td>399.0</td>
<td>531.0</td>
<td>596.5</td>
<td>1419</td>
</tr>
</tbody>
</table>
The absorption coefficient $\alpha(\nu)$ in Urbach’s exponential tail region is evaluated from the following equation

$$\alpha(\nu) = C \exp \left( \frac{h\nu}{\Delta E} \right)$$  --- (2)

Where $C$ is a constant and $\Delta E$ is the Urbach’s energy defined as the energy gap between localized tail states in the forbidden band gap [36]. Urbach tail plots drawn between $\ln(\alpha)$ and $\nu h$ are shown in Fig. 5.6. From these plots $\Delta E$ values are evaluated by taking the reciprocal of the slopes of the linear portion of the curves and are also presented in Table 5.3. Inset of Fig. 5.5 Tauc’s plots for optical band gap of ZBiG glasses doped with CoO.
Fig. 5.6 shows the variation of $E_g$ as well as $\Delta E$ with respect to dopant concentration of CoO.

![Graph showing variation of $E_g$ and $\Delta E$ with concentration of CoO.]

**Fig. 5.6** Urbach energy ($\Delta E$) of ZBiG glasses doped with CoO. Inset shows the variation of Urbach energy ($\Delta E$) and optical band gap ($E_g$) with concentration of CoO.

The values of some parameters, calculated from absorption bands, like full width at half maximum (FWHM), area etc., are presented in Table 5.4.
Table 5.4
Some Parameters evaluated from optical absorption spectra of ZBiG glasses doped with CoO.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Peak position (nm)</th>
<th>Area (arb.units)</th>
<th>FWHM (nm)</th>
<th>Peak Height (arb.units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>523.0</td>
<td>15.61</td>
<td>63.60</td>
<td>0.2511</td>
</tr>
<tr>
<td></td>
<td>596.0</td>
<td>7.15</td>
<td>34.58</td>
<td>0.2057</td>
</tr>
<tr>
<td></td>
<td>663.5</td>
<td>4.71</td>
<td>42.75</td>
<td>0.1120</td>
</tr>
<tr>
<td></td>
<td>527.5</td>
<td>21.52</td>
<td>61.72</td>
<td>0.3755</td>
</tr>
<tr>
<td>C2</td>
<td>596.0</td>
<td>12.55</td>
<td>34.63</td>
<td>0.3609</td>
</tr>
<tr>
<td></td>
<td>663.0</td>
<td>8.29</td>
<td>42.44</td>
<td>0.1977</td>
</tr>
<tr>
<td>C3</td>
<td>530.0</td>
<td>29.16</td>
<td>58.48</td>
<td>0.5504</td>
</tr>
<tr>
<td></td>
<td>597.0</td>
<td>20.48</td>
<td>34.63</td>
<td>0.5887</td>
</tr>
<tr>
<td></td>
<td>664.0</td>
<td>14.12</td>
<td>42.77</td>
<td>0.3345</td>
</tr>
<tr>
<td>C4</td>
<td>531.0</td>
<td>34.19</td>
<td>54.77</td>
<td>0.6987</td>
</tr>
<tr>
<td></td>
<td>597.0</td>
<td>29.11</td>
<td>35.05</td>
<td>0.8222</td>
</tr>
<tr>
<td></td>
<td>664.0</td>
<td>19.25</td>
<td>42.64</td>
<td>0.4567</td>
</tr>
<tr>
<td>C5</td>
<td>531.0</td>
<td>37.33</td>
<td>52.10</td>
<td>0.7869</td>
</tr>
<tr>
<td></td>
<td>596.5</td>
<td>33.48</td>
<td>35.02</td>
<td>0.9474</td>
</tr>
<tr>
<td></td>
<td>663.0</td>
<td>21.01</td>
<td>42.56</td>
<td>0.5038</td>
</tr>
</tbody>
</table>
5.4.2 FTIR spectra

FTIR spectra of all glasses recorded in order to identify the structural units in the glass network are shown in Fig. 5.7. The observed vibrational bands and the corresponding assignments are given in Table 5.5. The glass samples show four vibrations around 945 nm, 745 nm, 452 nm and 428 nm. The vibrational modes at 945 nm and 745 nm are blue shifted.

Fig. 5.7 FTIR spectra of ZBiG glasses doped with CoO.
Table 5.5

Assignment of absorption bands in the infrared spectra of the ZBiG glasses doped with CoO. (with a probable error of ±0.1 cm\(^{-1}\))

<table>
<thead>
<tr>
<th>C_0</th>
<th>C_1</th>
<th>C_2</th>
<th>C_3</th>
<th>C_4</th>
<th>C_5</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>428</td>
<td>410</td>
<td>427</td>
<td>419</td>
<td>421</td>
<td>424</td>
<td>Bi-O bonds in BiO(_6) units</td>
</tr>
<tr>
<td>452</td>
<td>465</td>
<td>481</td>
<td>484</td>
<td>459</td>
<td>488</td>
<td>Bi-O bonds in distorted BiO(_6) octahedra and ZnO(_4) units</td>
</tr>
<tr>
<td>745</td>
<td>749</td>
<td>745</td>
<td>748</td>
<td>743</td>
<td>741</td>
<td>Bi-O symmetrical stretching of BiO(_3) and Ge-O(^-) asymmetric stretching of GeO(_6) units</td>
</tr>
<tr>
<td>945</td>
<td>940</td>
<td>935</td>
<td>932</td>
<td>931</td>
<td>931</td>
<td>Bi-O stretching vibrations in BiO(_6) units and GeO(_4) units</td>
</tr>
</tbody>
</table>

5.4.3 Raman Spectra

Fig. 5.8 shows the Raman spectra of the all glass samples under investigation. The main Raman feature shifts (RF) and the corresponding bond vibrations are present in Table 5.6. A broad and intense RF is observed around 396 cm\(^{-1}\) and at 766 cm\(^{-1}\) with feeble features around ~ 564, ~ 891 and ~ 964 cm\(^{-1}\). By the addition of CoO the area of RF\(_{766}\) is increased with a slight blue shift and the area of RF\(_{964}\) is found to be decreased.
Whereas the area under Raman feature at 396 cm\(^{-1}\) is observed to be increased.

**Fig 5.8** Raman spectra of ZBiG glasses doped with CoO.
Table 5.6
Assignment of Raman Features (with a probable error of ±0.1 cm\(^{-1}\)) of ZBiG glasses doped with CoO.

<table>
<thead>
<tr>
<th>(C_0)</th>
<th>(C_1)</th>
<th>(C_2)</th>
<th>(C_3)</th>
<th>(C_4)</th>
<th>(C_5)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>306</td>
<td>306</td>
<td>307</td>
<td>304</td>
<td>307</td>
<td>307</td>
<td>Bi-O-Bi stretching vibrations in distorted BiO(_6) units</td>
</tr>
<tr>
<td>396</td>
<td>396</td>
<td>395</td>
<td>397</td>
<td>397</td>
<td>396</td>
<td>Doubly degenerate bending vibrations of Bi-O-Bi and symmetrical stretching vibrations of oxygen in Bi-O-Ge and Ge-O-Ge in GeO(_6) along with ZnO(_4) units</td>
</tr>
<tr>
<td>564</td>
<td>562</td>
<td>562</td>
<td>559</td>
<td>564</td>
<td>559</td>
<td>Bi-O vibrations in distorted BiO(_6) units</td>
</tr>
<tr>
<td>766</td>
<td>768</td>
<td>768</td>
<td>768</td>
<td>768</td>
<td>768</td>
<td>Symmetric stretching vibrations of Ge-O bonds in GeO(_4) units</td>
</tr>
<tr>
<td>891</td>
<td>881</td>
<td>891</td>
<td>889</td>
<td>888</td>
<td>902</td>
<td>Ge-O(^-) bonds associated with (Q^2) GeO(_4) units and Ge-O-Ge asymmetrical stretching</td>
</tr>
<tr>
<td>964</td>
<td>964</td>
<td>963</td>
<td>968</td>
<td>968</td>
<td>965</td>
<td>Ge-O(^-) bonds associated with (Q^3) GeO(_4) units</td>
</tr>
</tbody>
</table>

5.4.4 Dielectric properties

Fig. 5.9 shows the variation of dielectric constant \(\varepsilon'\) with the temperature of \(C_4\) sample at different frequencies. The variation of
dielectric constant with temperature for different concentrations of CoO at 100 KHz is shown in the inset of Fig. 5.9. Among all the samples C₀ sample has exhibited minimum value 13.78 for the dielectric constant ε' at 1 MHz and at the temperature 30°C. The sample C₅ has shown the maximum value 52.01 for ε' at 1 KHz and at the temperature 300°C.

**Fig.  5.9** Variation of dielectric constant ε' with temperature at different frequencies of C₄ sample. Inset shows the variation of ε' with temperature at 100 KHz for different concentrations of CoO in ZBiG glasses.
The variation of dielectric loss (tanδ) with temperature at 1 KHz for different concentrations of CoO is shown in Fig. 5.10 and its inset shows the temperature dependence of loss (tanδ) at different frequencies of C₃ sample. The curves of both pure and CoO doped glasses show distinct maxima in the dielectric loss (tanδ) versus temperature plot and such maxima is found to be shifted towards lower temperature region with increase in the concentration of CoO. Such maxima in the dielectric loss (tanδ), is the characteristic of relaxation of the dipoles present in the sample. Further, the variation of dielectric loss with temperature for different concentrations of CoO indicates a gradual increase in the broadening of relaxation curves. At the same time (tanδ)ₘₐₓ of relaxation curves is found to be increased with increase in the concentration of CoO.

The effective activation energy, w₆ for all glass samples is calculated for all the samples [37] using the following equation

\[ f = f_0 \exp \left( \frac{-W_d}{KT} \right) \]  -- (3)

Where \( f \) is the frequency and \( f_0 \) is a constant. The summary of data pertinent to loss (tanδ), activation energy for dipoles (A.E.) and breakdown strength for different concentrations of CoO are presented in Table 5.7 and from the observations it is found that \( w_d \) is maximum for C₀ sample and is decreased with CoO doping. Since insulating strength of the glass sample depends upon the electric field applied on it, the dielectric breakdown
The strength of the samples is determined. The value of the breakdown strength 12.92 KV/cm is obtained for $C_0$ sample and its value is found to be decreased with increase in the CoO concentration.

**Fig. 5.10** Variation of dielectric loss $\tan\delta$ with temperature at 1 KHz for different concentrations of CoO in ZBiG glasses. Inset shows the variation of loss $\tan\delta$ with temperature at different frequencies of $C_3$ sample
### Table 5.7

Summary of data on dielectric loss of ZBiG glasses doped with CoO at 1 KHz.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(Tan δ)_{max ave} x(10^{-1})</th>
<th>Temp. region of relaxation</th>
<th>AE for dipoles (eV)</th>
<th>Breakdown Strength (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₀</td>
<td>0.322</td>
<td>70-107</td>
<td>2.91</td>
<td>12.92</td>
</tr>
<tr>
<td>C₁</td>
<td>0.488</td>
<td>60-100</td>
<td>2.68</td>
<td>12.50</td>
</tr>
<tr>
<td>C₂</td>
<td>0.522</td>
<td>55-98</td>
<td>2.54</td>
<td>11.94</td>
</tr>
<tr>
<td>C₃</td>
<td>0.548</td>
<td>45-90</td>
<td>2.40</td>
<td>11.86</td>
</tr>
<tr>
<td>C₄</td>
<td>0.587</td>
<td>35-82</td>
<td>2.26</td>
<td>11.30</td>
</tr>
<tr>
<td>C₅</td>
<td>0.628</td>
<td>30-80</td>
<td>2.13</td>
<td>11.16</td>
</tr>
</tbody>
</table>

The a.c. conductivity values for all glasses at different temperatures and frequencies are evaluated [37] using the equation

\[ \sigma_{ac} = \omega \varepsilon_0 \varepsilon_{tan} \delta \tag{4} \]

where \( \omega \) is the angular frequency, \( \varepsilon_0 \) is the dielectric constant of vacuum. The variation of conductivity with 1/T of all investigated glasses at 10 KHz is shown in Fig. 5.11 and its inset shows the variation of conductivity with 1/T at different spot frequencies of C₂ sample. The activation energy (A.E.) for conduction in the linear region of log\( \sigma_{ac} \) with
$1/T$ plots, observed at higher temperature, has been evaluated. Such $\sigma_{ac}$ values at 70 $^\circ$C, density of defect energy states $N(E_F)$ and A.E. values for conduction of all the glass matrices are incorporated in Table 5.8.

![Graph showing variation of $\sigma_{ac}$ with $1000/T$ at 10 KHz for different concentrations of CoO in ZBiG glasses.](image)

**Fig. 5.11** Variation of $\sigma_{ac}$ with $1000/T$ at 10 KHz for different concentrations of CoO in ZBiG glasses. Inset of fig (a) shows the variation of $\sigma_{ac}$ with $1000/T$ for different frequencies of C$_2$ sample and fig(b) shows the variation of $\sigma_{ac}$ with Activation Energy.
Table 5.8

Summary of data on ac conductivity of ZBiG glasses doped with CoO at 10KHz.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_{a.c}$ at 70°C x(10^{-6}) (Ωcm)$^{-1}$</th>
<th>N(E_F) x (10^{20} (eV^{-1}/cm^{3})</th>
<th>AE for conduction (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_0</td>
<td>1.40</td>
<td>2.05 0.85 2.09</td>
<td>0.47</td>
</tr>
<tr>
<td>C_1</td>
<td>2.29</td>
<td>2.62 1.09 2.66</td>
<td>0.39</td>
</tr>
<tr>
<td>C_2</td>
<td>2.38</td>
<td>2.67 1.11 2.72</td>
<td>0.37</td>
</tr>
<tr>
<td>C_3</td>
<td>2.51</td>
<td>2.75 1.14 2.79</td>
<td>0.34</td>
</tr>
<tr>
<td>C_4</td>
<td>2.60</td>
<td>2.80 1.16 2.84</td>
<td>0.30</td>
</tr>
<tr>
<td>C_5</td>
<td>3.18</td>
<td>3.09 1.28 3.13</td>
<td>0.25</td>
</tr>
</tbody>
</table>

5.5 Discussion:

In general, the density of a glass is sensitive to the ionic size, atomic weight and amount of different elements present in the glass network [10, 38]. The observed decrease in the density and increase of molar volume by the doping of CoO is ascribed to the following: (i) due to the gradual decrease in the concentration of heavier and smaller Ge$^{4+}$ (0.39Å) ions and simultaneous increase in the lighter and larger Co$^{2+}$ (0.745 Å) ion concentration in the composition and/or (ii) formation of octahedral Ge$^{4+}$ [0.53 Å] ions than tetrahedral Ge$^{4+}$ [0.39 Å] ions in the glass network.
Further, the simultaneous decrease in density and increase in molar volume suggest the decrease of compactness of the glass structure with increase of CoO concentration. In other words doping of CoO opens the glass structure to some extent [39]. The other parameters such as mean Co$^{2+}$ ion concentration $N_i$, ion separation $R_{i}$ and polaron radius $R_p$ are helpful to understand the conducting nature of the glass network.

From Table 5.1, the values of the glass transition temperature $T_g$ and glass forming ability parameters viz., the ratios $(T_c - T_g)/T_g$, $T_g/T_m$, $(T_c - T_g)/T_m$ and $K_{gl}$, are observed to be decreased with increase in the concentration of CoO. Such values indicate higher thermal stability of the glasses. Normally, the decrease in bond length, cross-link density and closeness of packing of various structural groups in the glass matrix are responsible for such a decrease in these parameters with increase in the dopant concentration. The analysis of DTA data indicates with the increasing presence of CoO in the glass network, cobalt ions seem to exist in Co$^{2+}$ structural units, occupying glass modifier positions increase the cross-link density and weaken the mean bond strength, resulting a decrease in the rigidity of the glass network [29].

The observed two small peaks in $C_0$ sample at 685 and 827 nm [inset (a) of Fig 5.3] are attributed to $^3P_0 \rightarrow ^1D_2$ and $^3P_0 \rightarrow ^3P_2$ transitions of Bi$^+$ ions. Generally, such ions exist in the glass matrix due to thermal reduction
of Bi$^{3+}$ ions, into Bi$^{2+} \rightarrow$ Bi$^{+} \rightarrow$ Bi$^{0}$ bismuth radicals, which takes place during melting temperature at 1050$^0$ C [41-42]. The other absorption peaks observed at around 523 nm and 596 nm are attributed to $^4T_{1g} \rightarrow ^2T_{1g}(H)$, octahedral transition and $^4A_2(^4F) \rightarrow ^4T_1(^4P)$ tetrahedral (Td) transition of Co$^{2+}$ ions respectively. Besides the band in NIR region at 1434 nm is assigned to $^4A_2(^4F) \rightarrow ^4T_1(^4F)$ tetrahedral transition [43, 44] and a small shoulder at 663 nm is identified due to $^5T_2 \rightarrow ^5E$ transition of octahedral Co$^{3+}$ [45]. As the concentration of CoO ion is increased in the glass matrices, the area of tetrahedral band appears and is found to be decreased and at the same time area of octahedral band is observed to be increased. From this observation it is clear that majority of Co$^{2+}$ ions occupy octahedral positions with distortion due to John-Teller effect [46] which in turn decreases the rigidity of glass structure.

The absorption edge $\lambda_c$ observed at 386 nm for $C_0$ sample and increases with CoO doping suggests that the number of non-bridging oxygens (NBO’s) increases with increase in CoO concentration. This increase leads to degree of localization of electrons and hence the donor centers in the glass matrix. The study of variation of short wave length absorption edge (SWAE) and optical band gap in oxide glasses give information to understand the electron band structure. The observed red shift of SWAE with increase in the concentration of CoO results in
decreasing of optical band gap. The decrease in density, glass transition
temperature and optical band gap emphasize the same. Since Co-O bond
length is greater than Ge-O bond length, the doping of CoO effectively
opens the glass network. The addition of CoO increases the average bond
length which narrows the optical band gap [47]. Among the doped samples
C₁ sample has the minimum tail energy and it is found to be increased with
the increase of CoO concentration. The increase in Urbach energy is due to
the inducement of defects like fluctuations in bond angle distortions, wrong
bonds and color centers. As a result, the density of localized states N(E_F) of
these defects increases and leads to tailing of the states into the gap at the
band edges. This tailing also gives the evidence for decrease in E_g.

Vitreous GeO₂ exhibits IR transmission at ~ 915 cm⁻¹, ~ 750 cm⁻¹ and
~ 584 cm⁻¹ and are ascribed to asymmetric stretching vibrations of GeO₄
units, asymmetric vibrations of Ge-Ο⁻ bonds of GeO₆ and bending
vibrations of Ge₄-O-Ge₄ as reported previously [48, 51]. In the IR spectrum
of pure sample, the observed band at 945 cm⁻¹ is assigned to the stretching
vibrations of GeO₄ units. The band at 745 cm⁻¹ is due to degeneration of Bi-
O symmetrical stretching of BiO₃ units [49] as well as Ge-Ο⁻ asymmetric
stretching of GeO₆ units [51]. Another band at 452 cm⁻¹ is due to ZnO₄
structural units overlapped by Bi-O bonds in distorted BiO₆ units [52] and

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six-coordinated germanium ions [51]. A feeble band at 428 cm\(^{-1}\) is due to Bi-O bonds of different length in distorted BiO\(_6\) polyhedra [53].

From Fig. 5.7 we can observe that there is a slight decrease in area of band at 945 cm\(^{-1}\) and increase in area at 745 cm\(^{-1}\) as well as at 452 cm\(^{-1}\). From this it is concluded that with increase in concentration of CoO some of tetrahedral structural GeO\(_4\) units are found to be decreased and at the same time the octahedral structural GeO\(_6\) units are observed to be increased which results to the increase in the cross linking bonds such as Ge-O-Bi; Ge-O-Co; Co-O-Bi; Ge-O-Zn and Bi-O-Zn. Such changes are due to the increase of NBO’s. The red shift of band at 945 cm\(^{-1}\) is ascribed to the change in bond length when Ge-O is replaced by Co-O. Such structural change increases the conductivity of glass net work.

The Raman spectra of the glass samples show an intense peak around 396 cm\(^{-1}\) is assigned to the combination of ZnO\(_4\) structural units, Bi-O-Bi bending vibrations and symmetric stretching of bridging oxygens in Ge-O-Ge [53, 54]. The small shoulder at 564 cm\(^{-1}\) is due to Bi-O vibrations in BiO\(_6\) units [55]. Another observed intense peak at 766 cm\(^{-1}\) is assigned to symmetric stretching vibrations of Ge-O\(^-\) bonds in GeO\(_4\) units [56]. Further, two small peaks at 891 cm\(^{-1}\) and 964 cm\(^{-1}\) are ascribed to Ge-O-Ge asymmetrical stretching in GeO\(_4\) structural units [57, 58]. From Fig 5.8 it is observed that the area of RF at around 964 cm\(^{-1}\) is decreased and
RF at 396 cm$^{-1}$ is broadened and increased in area, which indicates the increase in octahedral units.

The inferences drawn from the analysis of FTIR spectra of the present glasses are also supporting that obtained from Raman spectra; such inferences indicate clearly the decrease in GeO$_4$ structural units and increase in GeO$_6$ structural units with increase in concentration of CoO. Hence, cobalt ions occupy octahedral positions in the glass structure, such ions act as a network modifier in decreasing the rigidity of glass matrix.

Among various polarizations (electronic, ionic, dipolar and space charge polarization) space charge polarization gives significant contribution to the dielectric constant and it depends on purity and perfection of the glass. The observed increase in the value of $\varepsilon'$, loss (tan$\delta$) and $\sigma_{ac}$ at any frequency are found to be increased with temperature. The activation energy decreases with increase in concentration of CoO, which is an indication of space charge polarization. The gradual increase in octahedrally positioned Co$^{2+}$ ions in the glass network leads to its modification. These ions weaken the glass network by creating bonding defects and create path ways for migration of ions that build up space charge polarization and leads to an increase in the dielectric parameters. This is also supported by the decrease in $T_g$ as well as decrease in the optical band gap energy, $E_g$. At higher concentration, cobalt ions in octahedral positions lead to more space
charge polarization and hence increase the disorder in the glass network [59].

The dielectric relaxation effects may be attributed to association of Co$^{2+}$ ions with a pair of Ge-O$^-$ groups and Bi$^{2+}$ ions with a pair of F$^-$ ions in analogy, such that the association of the divalent ion with a pair of cationic vacancies occurs in conventional glasses [60]. From Table 6 the increase in $(\tan \delta)_{\text{max,ave.}}$ and decrease in activation energy for dipoles with CoO content suggests that an increase in degree of freedom for dipoles to orient into the field direction leads to a decrease in rigidity of the glass network. The graph drawn between conductivity and activation energy (Inset of Fig 5.11) shows near linearity at higher temperature region suggests a random site model for conduction of the glasses [51]. This enhancement is directly related to the mobility of charge carriers. By correlating activation energy with mean separation ($R_i$), and polaron radius ($R_p$) such that, with increase in Co$^{2+}$ ion concentration, the mean site-to-site separation between cobalt ions decreases and polaron radius increases, which causes decrease in activation energy and increase of $\sigma_{\text{ac}}$ as reported previously [62].

The low temperature part of the conductivity can be explained on the basis of quantum mechanical tunneling model as reported by researchers [63]. The density of states $N(E_F)$ near Fermi level evaluated using the following equation[64]
\[ \sigma(\omega) = \eta^2 KT[N(E_F)]^2 \alpha^{-5} \omega \left[ \ln \left( \frac{V_{ph}}{\omega} \right) \right]^4 \quad \text{--- (5)} \]

where for Austin \( \eta = \pi/3 \) [63], Butcher \( \eta = 3.66 \frac{\pi^2}{6} \) [65] and Pollack \( \eta = \pi^4/96 \) [66] with the usual meaning of remaining symbols reported and presented in Table 5.7. The increase in the number of localized states, \( N(E_F) \) near Fermi level with \( \text{Co}^{2+} \) concentration indicates the increasing disorder in the glass network.

The breakdown strength of all the samples is determined at room temperature. Since the breakdown strength is inversely proportional to the value \( \varepsilon'(\tan\delta) \) the results suggests that the rate of increase of \( \varepsilon'(\tan\delta) \) with temperature is lowest for \( C_0 \) sample. Therefore, the experiments on dielectric breakdown strength of \( \text{ZnF}_2\text{-Bi}_2\text{O}_3\text{-GeO}_2:\text{CoO} \) glasses reveal that the modifying nature of the glasses increases with \( \text{CoO} \) concentration.

References:


