Zinc oxy fluoro borate glasses mixed with different concentrations of CoO (ranging from 0 to 2.0 mol %) were synthesized and subsequently crystallized. The scanning electron microscopy pictures indicated that the samples doped with higher concentration of CoO were embedded with randomly distributed crystal grains with the size ~ 10 μm. Differential scanning calorimetric studies have indicated that the prepared samples consist of multiple crystal phases. The X-ray diffraction patterns have indicated that the glass ceramic samples were composed of αZn(BO\(_2\))\(_2\), (Zn)\(_3\)(BO\(_3\))\(_2\), CoF\(_2\), CoF\(_3\), Co\(_3\)FB\(_2\)O\(_{13}\), ZnCo\(_2\)O\(_4\), Co\(_3\)O\(_4\) crystalline phases. The optical absorption and photoluminescence studies have indicated that there is a gradual increase tetrahedral cobalt ion concentration with increase of CoO concentration in the glass network. IR spectroscopic studies have pointed out increased degree of polymerization of the zinc oxy fluoro borate glass network with increase of CoO content. The analysis of results of dielectric properties (viz., dielectric constant, loss and ac conductivity measured over a range of frequency and temperature) indicated increase of insulating strength of the glass ceramics with increase of CoO content. Finally, the dielectric breakdown strength of the samples was measured at room temperature in air medium and it was found to increase from 12.9 to 19.2 kV/cm with increase of CoO from 0.2 to 2.0 mol%. This value was found to be within the range of breakdown strength required for a transparent dielectric layer to be used in the plasma display panels. The reasons for such increase of breakdown strength were discussed quantitatively in terms of dielectric parameters with aid of data on spectroscopic properties.
Insulating properties of CoO doped zinc oxy fluoro borate glass ceramics for application in plasma display panels

5.1 Introduction

Glass ceramic materials possess good mechanical, electrical and thermal properties, high chemical durability and low coefficient of thermal expansion with no crack growth inside. In recent years, several studies were reported on the crystallization of the glass materials and its influence on the physical properties[1-4]. Glass ceramic materials can retain the transparency if average diameter of crystalline grains (formed in the bulk material during the crystallization) is less than the wavelengths of visible and NIR spectral regions. Further, the glass ceramic materials are more stable against high intense UV, visible and even laser beams and can withstand to the high voltages when compared with the amorphous materials.

Among different glass systems ZnO mixed borate or silicate glasses posses low specific heat, high thermal conductivity and ZnO in these glasses dissipates heat more rapidly when compared with that of glasses containing heavy metal oxide modifiers like BaO and PbO. Further, dielectric breakdown strength of ZnO mixed glasses was found to be abnormally high probably because the electrons in the outer most shell of Zn\(^2+\) cations is 18. For this reason thin layers of these glasses are being extensively used as insulating layers in plasma display panels [5, 6].
The breakdown strength of these glasses can further be improved if the glasses are crystallized. Catalysts generally used for controlling crystallization processes giving rise to enormous numbers of nucleation centers in the original glass, are gold, silver, platinum or the oxides of transition metals like Ti, Cr, Mn, Ce, V, Fe, Co, Ni, Zr, etc. Among them, the addition of CoO as crystallizing agent is an added advantage for these materials because the interaction between the glass ceramic network and the cobalt ions was reported to have very strong electron phonon interaction and facilitate for more dissipation of heat. As a result the breakdown strength of the materials would further be enhanced [7]. Further, glasses containing cobalt ions are good candidates for nonlinear optical absorbers needed for passive modulations of laser beams [8]. These materials are also considered as useful materials for Q-switching devices [9] since they exhibit strong luminescence in the visible and near-infrared regions.

In glass materials, cobalt ions exist in two stable valence states, viz., $\text{Co}^{2+}$ and $\text{Co}^{3+}$. $\text{Co}^{2+}$ ions participate in the glass network in octahedral and tetrahedral co-ordinations. The concentration of $\text{CoO}_4$ and $\text{CoO}_6$ structural units depends upon the composition of host glass as well as on the content of CoO in the glass matrix. The relative variations in the concentration of these two structural units of cobalt are expected to change the insulating character of the glass to large extent. $\text{ZnF}_2$, like any other alkali or alkaline earth fluorides, when added to the glass matrices like zinc borate, is excepted to decrease the viscosity and liquidus
temperature to a substantial extent and further, it was predicted to act as an effective mineralizer of the glass [10].

The objectives of this investigation are: (i) to synthesize ZnO–ZnF$_2$–B$_2$O$_3$ glass and to crystallize them with different concentration of CoO as nucleant, (ii) to characterize them by XRD, SEM and EDS techniques, (iii) to study their spectroscopic properties viz., optical absorption, IR and luminescence to assess the structural changes taking place in the glass ceramic due to varying concentration of nucleating agent and (iv) finally, we have studied dielectric properties (over a long range of frequency and temperature) and dielectric breakdown strength of the material to estimate the change in its insulating strength and identified optimal concentration of CoO (with the aid of the data on spectroscopic properties) that makes the glass suitable for transparent insulating devices like dielectric layer useful for plasma display panels.

5.2 Brief review of the previous work on the glasses and glass ceramics containing cobalt ions

Kurajica et al. [11] have reported the evolution of structural and optical properties in the course of thermal evolution of sol–gel derived cobalt–doped gahnite. These authors have interpreted the spectra as a progressive reduction of Co$^{3+}$ to Co$^{2+}$ ions at higher temperatures. Carmona et al. [12] have reported Cobalt (II) environment characterization in sol–gel thermo chromic sensors.
Yasemin Caglaret [13] investigated the Structural, optical and electrical properties of Sol–gel derived nanostructure of undoped and cobalt doped ZnO. In this investigation this author found that the doping of ZnO with Co caused a decrease in particle size and crystallinity while it led to an increase in the band gap. Mekki et al. [14] have reported the results of XPS and magnetization studies of cobalt sodium silicate glasses. In this study this author has reported that indicate that the exchange interaction is antiferromagnetic and it increased with increasing CoO in the glass. Sławomir et al. [15] have reported The presence of different oxidation states of cations in optical hosts on the base of Co:SrLaGa$_3$O$_7$. In this study it was reported that Co–doping with vanadium increased the radiation hardness of Co:SrLaGa$_3$O$_7$ crystal. Volk et al. [16] have reported stimulated emission of Co$^{2+}$ doped glass–ceramics. Duan et al. [17] have reported the X-ray photoelectron spectroscopy studies of Co-doped ZnO–Ga$_2$O$_3$–SiO$_2$ nano-glass–ceramic composites. Chen et al. [18] have investigated Spectroscopic properties of Co$^{2+}$ ions in La$_2$O$_3$–MgO–Al$_2$O$_3$–SiO$_2$ glass-ceramics. Kang et al. [19] have studied structural transformations of nanometer sized crystals in CoO–doped β-eucryptite-based glass-ceramics.

Bhattacharya et al. [20] 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. [21] 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. [22] have prepared silver phosphate mixed with cobalt chloride and have measured the electrical conductivity of these samples. Bergo et al. [23] have reported the dielectric properties of $P_2O_5$-$Na_2O$-$Li_2O$ glasses containing $WO_3$, $CoO$ or $Fe_2O_3$ 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. [24] 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. [25] have reported the effect of cobalt ions on the EPR and d.c. conductivity in vanadyl doped $CoO$-$M_2O$–$B_2O_3$ ($M=$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\textsubscript{2}O ratio. Kojima et al. [26] have reported electron spin resonance spectra of high-spin Co\textsuperscript{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\textsuperscript{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 [27] have reported spectroscopic properties of Mn\textsuperscript{2+}, Co\textsuperscript{2+} and Ni\textsuperscript{2+} in B\textsubscript{2}O\textsubscript{3}-ZnO-PbO glasses. In this study, they have reported red emission due to \( ^2\text{E}(\,^2\text{G}) \rightarrow ^4\text{A}_2(\,^4\text{F}) \) tetrahedral transition of Co\textsuperscript{2+} ions in this glass matrix. Ryba-Romanowski et al. [28] 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\textsuperscript{2+} and Co\textsuperscript{3+} ionic states. Mansour et al. [29] have prepared CoO-TeO\textsubscript{2}-V\textsubscript{2}O\textsubscript{5} glass system and have reported the results of studies on dc conductivity, density and molar volume. Elbatal et al. [30] 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\textsuperscript{+} 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. [31] have prepared two series of P\textsubscript{2}O\textsubscript{5}-based oxide glasses containing at the same time the MoO\textsubscript{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. Mońcke and Ehrt [32] 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$^{2+}$)$_2^+$ in all glasses. Esposito et al. [33] 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(OC$_2$H$_5$)$_4$ 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. [34] 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 $^4T_1(^4P) \rightarrow ^4A_2(^4F)$ and $^4T_1(^4P) \rightarrow ^4T_2(^4F)$ transitions of tetrahedral Co$^{2+}$, respectively. Bhatty et al. [35] 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 Tl₂O content of the glass. Denisov et al. [36] 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. [37] have also reported similar studies in magnesium-aluminum spinel nanocrystallites containing cobalt ions. These authors have measured the relaxation time of ⁴A₂ → ⁴T₁(⁴F) transition of Co²⁺ ions as 450 ± 150 ns. Kim et al. [38] have prepared cobalt (Co) and tantalum (Ta) co-substituted BiFeO₃ polycrystalline ceramics and investigated the dielectric and magnetic properties. Sakuda et al. [39] have fabricated solid-state lithium secondary batteries using LiCoO₂ particles coated with amorphous Li₂O–TiO₂ films as an active material and Li₂S–P₂S₅ glass-ceramics as a solid electrolyte and investigated electrochemical performance.

5.3 Characterization

A particular composition (10–x) ZnO–30ZnF₂–60B₂O₃: xCoO with six values of x ranging from 0.2 to 2.0 was chosen for the present study. The detailed compositions of the glasses used in this investigation were as follows:

CC₂: 9.8ZnO–30ZnF₂–60B₂O₃: 0.2CoO
CC₄: 9.6ZnO–30ZnF₂–60B₂O₃: 0.4 CoO
CC₆: 9.4ZnO–30ZnF₂–60B₂O₃: 0.6 CoO
CC₈: 9.2ZnO–30ZnF₂–60B₂O₃: 0.8 CoO
CC₁₀: 9.0ZnO–30ZnF₂–60B₂O₃: 1.0 CoO
CC_{20}: 8.0\text{ZnO} – 30\text{ZnF}_2 – 60\text{B}_2\text{O}_3: 2.0 \text{CoO}

5.3.1 Physical properties

From the measured values of the density and average molecular weight $\bar{M}$ of the samples, various other physical parameters such as cobalt ion concentration, $N_i$, mean cobalt ion separation $R_i$, polaron radius $r_p$ in ZnO–ZnF$_2$–B$_2$O$_3$: CoO glass ceramic samples were evaluated and presented in Table 5.1. The density of the samples was observed to increase slightly with the concentration of CoO.

5.3.2 Scanning electron microscopy (SEM) and EDS

The SEM pictures of the ZnO–ZnF$_2$–B$_2$O$_3$ glasses crystallized with different concentrations of CoO were shown in Fig. 5.1. The pictures exhibited gradual crystallinity with increase of CoO content. A clear crystal grains of size $\sim 10 \ \mu\text{m}$ could be were observed in the photographs of the samples crystallized with higher concentration of CoO. The close observation of the pictures further suggested a gradual increase in the volume fraction of crystallites in the samples with increasing concentration of CoO.
### Table 5.1
Physical Parameters of ZnO–ZnF$_2$–B$_2$O$_3$: CoO glass ceramics

<table>
<thead>
<tr>
<th>Glass ceramic</th>
<th>Density (g/cm$^3$)</th>
<th>Dopant ion Conc. $N_i$ ($\times 10^{20}$ ions/cm$^3$)</th>
<th>Inter ionic distance (Å$^o$)</th>
<th>Polaron radius (Å$^o$)</th>
<th>Refractive index(n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC$_2$</td>
<td>2.959</td>
<td>0.44</td>
<td>6.10</td>
<td>2.46</td>
<td>1.638</td>
</tr>
<tr>
<td>CC$_4$</td>
<td>2.962</td>
<td>0.88</td>
<td>4.84</td>
<td>1.95</td>
<td>1.641</td>
</tr>
<tr>
<td>CC$_6$</td>
<td>2.971</td>
<td>1.32</td>
<td>4.23</td>
<td>1.70</td>
<td>1.643</td>
</tr>
<tr>
<td>CC$_8$</td>
<td>2.978</td>
<td>1.77</td>
<td>3.84</td>
<td>1.55</td>
<td>1.648</td>
</tr>
<tr>
<td>CC$_{10}$</td>
<td>2.982</td>
<td>2.22</td>
<td>3.56</td>
<td>1.43</td>
<td>1.652</td>
</tr>
<tr>
<td>CC$_{20}$</td>
<td>2.992</td>
<td>1.53</td>
<td>2.81</td>
<td>1.13</td>
<td>1.658</td>
</tr>
</tbody>
</table>

The chemical makeup of the glass ceramics was characterized by electron dispersive spectroscopy (EDS); the energy analysis of the C$_{10}$ glass ceramic (Fig. 2) materials indicated zinc, boron, cobalt, fluorine and oxygen elements were present in various crystalline phases.

#### 5.3.3 X-Ray diffraction (XRD)

XRD studies of ZnO–ZnF$_2$–B$_2$O$_3$:CoO glass ceramics indicated that these materials comprise of different crystal phases. Some of the important crystal phases include $\alpha$Zn(BO$_2$)$_2$, (Zn)$_3$(BO$_3$)$_2$, CoF$_2$, CoF$_3$, Co$_3$FB$_7$O$_{13}$, ZnCo$_2$O$_4$, Co$_3$O$_4$ [40]. The presence of diffraction peaks due to CoF$_2$ and
Co$_3$FB$_7$O$_{13}$ crystal phases at 2θ=26.62$^\circ$ and 29.59$^\circ$ indicated that the cobalt ions existed predominantly in Co$^{2+}$ state in the glass ceramic. However, the presence of diffraction peaks due to CoF$_3$ (2θ = 28.55$^\circ$, 39.79$^\circ$) and ZnCo$_2$O$_4$ (2θ = 31.21$^\circ$, 36.85$^\circ$) crystalline phases indicate that a part of cobalt ions existed in Co$^{3+}$ state. The X-ray diffractogram for one of the samples, viz., CC$_2$, was shown in Fig. 5.3 (a) and for all the glass ceramics were presented in (Fig. 5.3(b)). The close observation of the pattern clearly indicated a considerable increase in the intensity and full width at half maximum of peaks due to CoF$_2$, Co$_3$FB$_7$O$_{13}$ and Co$_3$O$_4$ crystalline phases with the increase of CoO content.

**5.3.4 Differential Scanning Calorimetric studies**

Differential scanning calorimetric (DSC) curves for ZnO–ZnF$_2$–B$_2$O$_3$ glasses crystallized with different concentration of CoO were presented in Fig. 5.4. The thermograms of all glass–ceramic samples exhibited a weak glass transitions with the inflection point situated between 580 and 620 °C accompanied by multiple exothermic peaks at the three steps of crystallization temperatures. From the DSC traces the values of $T_g$ (inflection point), $T_c$ (central peak crystallization) and ($T_c - T_g$), were evaluated and presented in Table 5.2. With the increasing content of the nucleating agent, the value of ($T_c - T_g$) exhibited a decreasing trend. The enthalpy associated with the
Fig. 5.1 SEM pictures of ZnO–ZnF$_2$–B$_2$O$_3$: CoO glass – ceramics
Fig. 5.5 EDS spectra of glass ceramic CC$_{10}$
Fig. 5.3(a). XRD pattern of ZnO–ZnF$_2$–B$_2$O$_3$:CoO glass ceramics (CC$_2$)
crystallization peaks with the concentration of crystallizing agent seemed to be increasing with increase in the concentration of nucleating agent.

**Fig. 5.3(a).** XRD patterns of ZnO–ZnF$_2$–B$_2$O$_3$–CoO glass ceramics
Fig. 5.4 DSC patterns of ZnO–ZnF$_2$–B$_2$O$_3$ :CoO glass ceramics
Table 5.2
Summary of data on differential scanning calorimetric studies of ZnO–ZnF₂–B₂O₃ glass ceramics doped with different concentration of CoO.

<table>
<thead>
<tr>
<th>Glass ceramic</th>
<th>Glass transition temperature (K) (Inflection) (Tᵥ)</th>
<th>Crystallization temperature (K) (peak) (Tₕ)</th>
<th>Tᵥ — Tₕ</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC₂</td>
<td>588</td>
<td>675</td>
<td>87</td>
</tr>
<tr>
<td>CC₄</td>
<td>592</td>
<td>680</td>
<td>88</td>
</tr>
<tr>
<td>CC₆</td>
<td>598</td>
<td>692</td>
<td>94</td>
</tr>
<tr>
<td>CC₈</td>
<td>603</td>
<td>705</td>
<td>102</td>
</tr>
<tr>
<td>CC₁₀</td>
<td>611</td>
<td>721</td>
<td>110</td>
</tr>
<tr>
<td>CC₂₀</td>
<td>620</td>
<td>735</td>
<td>115</td>
</tr>
</tbody>
</table>

5.4 Results

5.4.1 Optical absorption spectra

The optical absorption spectra of ZnO–ZnF₂–B₂O₃: CoO glass ceramics recorded at room temperature in the spectral range 300–1700 nm were presented in Fig. 5.5. The absorption edge observed at 421 nm for glass ceramic CC₂ was observed to shift gradually towards the shorter wavelength with increasing the content of CoO. The spectrum of CC₂, exhibited three principal absorption bands at 530 nm, 563 nm and at about 1378 nm. Out of
Fig. 5.5. Optical absorption of ZnO–ZnF₂–B₂O₃:CoO glass ceramics
Fig. 5.6(a). Tauc plots of ZnO–ZnF$_2$–B$_2$O$_3$:CoO glass ceramics

Fig. 5.6(b) $(\alpha \nu) v s \nu$ plots of ZnO–ZnF$_2$–B$_2$O$_3$:CoO glass ceramics
**Table 5.3**
Absorption band positions and optical band gaps of ZnO–ZnF$_2$–B$_2$O$_3$: CoO glass ceramics

<table>
<thead>
<tr>
<th>Glass ceramic</th>
<th>Cut-off Wavelength (nm)</th>
<th>Band positions (nm)</th>
<th>Optical Band gap (eV)</th>
<th>Direct band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$^4T_{1g}(F)\rightarrow^2T_{1g}(H)$</td>
<td>$^4A_2(^4F)\rightarrow^4T_{1}(^4P)$</td>
<td>$^5T_{2g}\rightarrow^5E_g(H)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(O$_h$) (nm)</td>
<td>(T$_d$) (nm)</td>
<td>(O$_h$) (nm)</td>
</tr>
<tr>
<td>CC$_2$</td>
<td>421</td>
<td>530</td>
<td>562</td>
<td>669</td>
</tr>
<tr>
<td>CC$_4$</td>
<td>405</td>
<td>526</td>
<td>566</td>
<td>663</td>
</tr>
<tr>
<td>CC$_6$</td>
<td>380</td>
<td>523</td>
<td>570</td>
<td>659</td>
</tr>
<tr>
<td>CC$_8$</td>
<td>365</td>
<td>519</td>
<td>573</td>
<td>657</td>
</tr>
<tr>
<td>CC$_{10}$</td>
<td>350</td>
<td>518</td>
<td>576</td>
<td>652</td>
</tr>
<tr>
<td>CC$_{20}$</td>
<td>335</td>
<td>513</td>
<td>580</td>
<td>649</td>
</tr>
</tbody>
</table>
these, the band at 530 nm was identified as being due to $T_{1g}(F) \rightarrow 2T_{1g}(H)$ octahedral transition, whereas the other two bands observed at 563 nm and 1378 nm were attributed to $^4A_2(^4F) \rightarrow ^4T_1(^4P)$ and $^4A_2(^4F) \rightarrow ^4T_1(^4F)$ tetrahedral transitions, respectively, of Co$^{2+}$ ions[41]. Additionally, a distinct kink at about 669 nm predicted due to $^4T_{2g} \rightarrow ^5E_g$ octahedral transition of Co$^{3+}$ ions was also located in the spectrum of this glass. As the concentration of CoO was increased, the octahedral band positions were shifted towards the shorter wavelength, whereas tetrahedral band positions were shifted towards the longer wavelength with increasing intensity (Table 5.3).

From the observed absorption edges, we have evaluated the optical band gap ($E_o$) of these samples by drawing Tauc plots [42] between $(\alpha \omega)^{1/2}$ vs $\omega$ and $(\alpha \omega)^2$ vs $\omega$ as described in earlier chapters. Figs. 5.6 (a) and 5.6 (b) represent such plots of all these glass ceramics.

From the extrapolation of the linear portion of the curves, the values of both indirect and direct optical band gap $E_o$ were determined. The summary of the data on various band positions of optical absorption spectra and both indirect and direct optical band gap $E_o$ of these glass ceramics were presented in Table 5.3. Both of these values were found to increase with the increase of CoO content.

For assigning the bands to their corresponding transitions of cobalt ions and to evaluate crystal field parameters we have drawn TS diagram for $d^7$ ion.
Fig. 5.7 represents such diagram for one of the glass ceramics viz., CC$_{20}$ along with corresponding optical absorption spectrum. The Crystal field parameters viz., B, C and D$_q$ were evaluated using energies of these transitions and were presented in Table 5.4.

### 5.4.2 Photoluminescence spectra

The photoluminescence emission spectra of ZnO–ZnF$_2$–B$_2$O$_3$: CoO glass ceramics recorded (at room temperature) excited at the wavelength corresponding to their cut-off wavelength were presented in Fig. 5.8. The spectra of each sample exhibited three emission bands in the spectral region 400–900 nm. Among these, a broad and intense emission band was observed at about 500 nm in the spectra of all the glass ceramics including CoO free sample. This band was envisaged due to free-excitons’ recombination in the energy gap [43]. The remaining two emission bands in the regions 600–700 nm and 800–900 nm were identified as being due to $^4T_1(^4P)$ → $^4A_2(^4F)$ and $^4T_1(^4F)$ → $^4A_2(^4F)$ tetrahedral transitions of Co$^{2+}$ ion, respectively [44]. As the concentration of CoO is increased no significant change was observed in the exciton recombination band, but the half width and intensity of latter bands was observed to increase with shifting of peak positions towards slightly longer wavelength.
Fig. 5.7(a). Tanabe–Sugano diagram and corresponding optical spectrum for glass ceramic CC$_{20}$
Fig. 5.7(b) Energy level scheme describing the absorption process in cobalt ion doped ZnO–ZnF₂–B₂O₃:CoO glass ceramic CC₂₀
5.4.3 Infrared transmission spectra

As a part of having some structural assessment that may help in evaluating the insulating character of the glass ceramic, we have also recorded infrared transmission spectra of ZnO–ZnF$_2$–B$_2$O$_3$;CoO glass ceramics in the region 400–1600 cm$^{-1}$ (Fig. 5.9). IR spectra of all the glass ceramic samples exhibited a band in the region 1200–1600 cm$^{-1}$ identified as being due to the stretching relaxation of the B–O bond of the trigonal BO$_3$ units. Another conventional band due to the vibrations of BO$_4$ units was also observed in the spectral region 1200–800 cm$^{-1}$. The spectra further exhibited a band due to B–O–B linkages at about 670 cm$^{-1}$ [45, 46]. The band due to the vibrations of ZnO$_4$ tetrahedral units was detected at about 490 cm$^{-1}$ in the spectra of all these samples [47, 48]. Interestingly, two weak kinks, presumed to be due to the vibrations of Co$^{III}$–O were also located in these spectra in the region 540–600 cm$^{-1}$ [49]. As the concentration of CoO
Table 5.4
Crystal field parameter and Racah parameters of ZnO–ZnF$_2$–B$_2$O$_3$: CoO glass ceramics

<table>
<thead>
<tr>
<th>Glass ceramic</th>
<th>Crystal Field Parameter $D_q$ (cm$^{-1}$)</th>
<th>Racah parameters</th>
<th>Nephelauxetic ratio $\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$B$ (cm$^{-1}$)</td>
<td>$C$ (cm$^{-1}$)</td>
</tr>
<tr>
<td>CC$_2$</td>
<td>- 421.6</td>
<td>842</td>
<td>3898</td>
</tr>
<tr>
<td>CC$_4$</td>
<td>- 419.7</td>
<td>838</td>
<td>3880</td>
</tr>
<tr>
<td>CC$_6$</td>
<td>- 418.9</td>
<td>832</td>
<td>3852</td>
</tr>
<tr>
<td>CC$_8$</td>
<td>- 415.1</td>
<td>826</td>
<td>3824</td>
</tr>
<tr>
<td>CC$_{10}$</td>
<td>- 416.5</td>
<td>819</td>
<td>3792</td>
</tr>
<tr>
<td>CC$_{20}$</td>
<td>- 415.7</td>
<td>814</td>
<td>3769</td>
</tr>
</tbody>
</table>
Fig. 5.8. Photo luminescence of ZnO–ZnF$_2$–B$_2$O$_3$:CoO glass ceramics
Fig. 5.9. IR spectra of ZnO–ZnF$_2$–B$_2$O$_3$:CoO glass ceramics
was increased, the vibrational band due to BO\textsubscript{4} structural units was observed to grow at the expense of band due to BO\textsubscript{3} units. Additionally, the BO\textsubscript{4} band exhibited a considerable shift towards lower wavenumber. The summary of various band positions of the IR spectra of these glass ceramics was furnished in Table 5.5.

**5.4.4 Dielectric properties and Breakdown Strength**

The room temperature dielectric constant, $\varepsilon'$ at 1 MHz of 0.2 mol% CoO doped glass was measured to be 16.4. With the gradual increase of CoO up to 2.0 mol%, the value of $\varepsilon'$ decreased to 15.2. The variation of dielectric constant

<table>
<thead>
<tr>
<th>Glass ceramic</th>
<th>Band positions</th>
<th>ZnO\textsubscript{4} units</th>
<th>Co\textsuperscript{III} – O groups</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BO\textsubscript{3}</td>
<td>BO\textsubscript{4}</td>
<td>B-O-B</td>
</tr>
<tr>
<td>CC\textsubscript{2}</td>
<td>1369</td>
<td>1063</td>
<td>682</td>
</tr>
<tr>
<td>CC\textsubscript{4}</td>
<td>1373</td>
<td>1057</td>
<td>683</td>
</tr>
<tr>
<td>CC\textsubscript{6}</td>
<td>1377</td>
<td>1050</td>
<td>687</td>
</tr>
<tr>
<td>CC\textsubscript{8}</td>
<td>1381</td>
<td>1047</td>
<td>688</td>
</tr>
<tr>
<td>CC\textsubscript{10}</td>
<td>1383</td>
<td>1037</td>
<td>690</td>
</tr>
<tr>
<td>CC\textsubscript{20}</td>
<td>1386</td>
<td>1033</td>
<td>695</td>
</tr>
</tbody>
</table>
with frequency measured at different temperatures exhibited a constant value \( \varepsilon'(\omega) \) which normally results in a rapid polarization processes occurring in the glasses under applied field [50–52]. With increase in temperature the dielectric constant was found to increase with largest values at lower frequencies of all the glass ceramics. In Figs. 5.10 and 5.11, the dispersion of dielectric constant, \( \varepsilon'(\omega) \) with temperature and frequency, respectively, of glass ceramic CC\(_{20}\) were presented. A comparison plot of dielectric constant with temperature measured at a frequency of 1 kHz of all the samples was presented in the inset of Fig. 5.10. Interestingly, dielectric constant was found to decrease with increase of CoO content.

The dielectric loss, \( \tan \delta \), dispersions with temperature and frequency for the glass ceramic CC\(_{10}\) were presented in Figs. 5.12 and 5.13, respectively. The loss dispersion curves exhibited relaxation character for these glass ceramics [50, 53]. The dielectric loss variation with temperature measured at a frequency of 10 kHz was presented in the inset of Fig. 5.12. The figure exhibited decrease \( (\tan \delta)_{\text{max}} \) of relaxation curves with increase of CoO content. The curves were also found to be narrowed with content of CoO and the region of dielectric relaxation in the studied frequency range was found to be shifted
Fig. 5.10. Variation of dielectric constant $\varepsilon'(\omega)$ with temperature for the glass ceramic (CC$_{20}$) at different frequencies. Inset represents variation of dielectric constant $\varepsilon'(\omega)$ with temperature for different glass ceramics measured at 1 KHz.
Fig. 5.11. Variation of dielectric constant $\varepsilon'(\omega)$ with frequency for the glass ceramic (CC$20$) at different temperatures.
Fig. 5.12. Variation of dielectric loss $\tan \delta$ with temperature for the glass ceramic (CC$_{10}$) at different frequencies. Inset represents variation of dielectric loss $\tan \delta$ with temperature for different glass ceramics measured at 10 KHz.
towards higher temperatures (Table 5.6). Following the Boltzmann’s relation, $f = f_0 \exp \left( -\frac{W_d}{k_B T} \right)$, ($f_0$ is the constant, $k_B$ is the Boltzmann’s constant, $T$ is the absolute temperature and $f$ is the relaxation frequency), the effective activation energy $W_d$, for the dipoles was evaluated for all the glass ceramic samples and
presented in Table 5.6; the activation energy was found to be increased with increase of CoO content.

For the better understanding of electrical relaxation behavior in ion conducting materials of the titled glasses, we have evaluated real and imaginary electric moduli, $M'(\omega)$ and $M''(\omega)$ dispersion, from real and imaginary parts of complex dielectric constant at different temperatures for all these samples as explained in earlier chapter. The dependence of $M'(\omega)$ and $M''(\omega)$ with the frequency and temperature for one of the glass ceramics (viz., CC$_8$) was presented in Figs. 5.14 (a) and (b), respectively. These figures clearly exhibited the relaxation feature for dielectric properties of the studied glasses. The real part of electric modulus, $M'(\omega)$, increased with increasing temperature and at sufficiently high temperature reached a plateau that corresponds to the limiting value of $M_\infty$. The maximum of $M'(\omega)$ peak was shifted to higher frequency with increasing temperature. The plots of electric moduli versus frequency for other glasses demonstrated similar behavior. The frequency region below the peak maximum of $M''(\omega)$
Fig. 5.14. (a) The frequency dependency of $M'$ at different temperatures for CC$_8$ glass ceramic.
(b) The frequency dependency of $M''$ at different temperatures for CC$_8$ glass ceramic.
normally represent long range distances of the mobile charge carriers, whereas at frequency above peak maximum $M''(\omega)$, the carriers are spatially confined to potential wells, being mobile on short distances and making only localized motion within the wells. The point of intersection of two curves at $(M'')_{\text{max}}$ represents characteristic frequency which is equal to the relaxation frequency described by by $\omega_{\text{max}} = 1/\tau_M$, where $\tau_M$ describes the relaxation time for the dipoles. The relaxation times, $\tau_M$, evaluated for all glasses in the similar way at 413 K and were presented in Table 5.6. The value of $\tau_M$ was found to be increasing with increase of CoO content (Table 5.6).

In Fig. 5.15, isotherms of ac conductivity dispersion were plotted for CC$_8$ glass ceramic, whereas in Fig. 5.16 ac conductivity vs inverse temperature at different frequencies for the same sample was presented. The frequency dependence of ac conductivity at a given temperature exhibited a universal feature [54] where at low frequency region and higher temperature range the conductivity is independent of temperature. At the same time at higher frequency and lower temperature conductivity exhibited dispersion in power law fashion. The dependence of ac conductivity with the content of CoO at any given frequency and temperature exhibited the maximal effect at about 0.2 mol% and with the increase of CoO content from 0.2 to 2.0 mol%, the conductivity was found to be decreased (inset (a) of Fig. 5.15). From the plots of log $\sigma_{\text{ac}}$ vs $1/T$, we have evaluated the activation energy, $W_{\text{ac}}$ for the
conduction in the high temperature region over which a near linear dependence of \( \log \sigma_{ac} \) with \( 1/T \) could be observed and presented in Table 5.7.

Table 5.6

<table>
<thead>
<tr>
<th>Glass ceramic</th>
<th>Temp. Region of relaxation (K)</th>
<th>A.E. for dipoles, ( W_d ) (eV)</th>
<th>Relaxation Time ( \tau_M ) (( \mu s ))</th>
<th>Breakdown strength (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC_2</td>
<td>356–412</td>
<td>1.56</td>
<td>130</td>
<td>12.92</td>
</tr>
<tr>
<td>CC_4</td>
<td>369–421</td>
<td>1.78</td>
<td>138</td>
<td>13.85</td>
</tr>
<tr>
<td>CC_6</td>
<td>378–428</td>
<td>1.93</td>
<td>142</td>
<td>14.63</td>
</tr>
<tr>
<td>CC_8</td>
<td>385–432</td>
<td>2.11</td>
<td>159</td>
<td>16.25</td>
</tr>
<tr>
<td>CC_10</td>
<td>396–440</td>
<td>2.36</td>
<td>165</td>
<td>17.94</td>
</tr>
<tr>
<td>CC_20</td>
<td>413–453</td>
<td>2.79</td>
<td>172</td>
<td>19.21</td>
</tr>
</tbody>
</table>

The variations of activation energy and ac conduction with the concentration of CoO exhibited reversal trends (inset (a) of Fig. 5.16). However, the plots of \( \log \sigma_{ac} \) vs activation energy for conduction, exhibited a near-linear relationship (inset (b) of Fig. 5.16)). The value of dielectric breakdown strength was found to be increased from 12.9 to 19.2kV/cm (CC_20) with increase of CoO concentration (Table 5.6).
Fig. 5.15. Variation of ac conductivity with frequency for the glass ceramic CC$_8$. 

![Graph showing variation of ac conductivity with frequency for different temperatures.](image-url)
Fig. 5.16. Variation of ac conductivity with 1/T for the glass ceramic CC₈. Inset (a) variation of $\sigma_{ac}$ (measured at 573 K) and activation energy with the concentration of CoO. Inset (b) variation of $\sigma_{ac}$ with activation energy in high temperature region.
Table 5.7
Summary data on ac conductivity studies of ZnO–ZnF$_2$–B$_2$O$_3$ glass ceramics doped with different concentration of CoO

<table>
<thead>
<tr>
<th>Glass ceramic</th>
<th>A.E. for conduction $W_{ac}$ (eV)</th>
<th>Exponent $s$</th>
<th>N(E$_F$) $\times 10^{21}$, eV$^{-1}$/cm$^3$ (± 0.01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC$_2$</td>
<td>0.57</td>
<td>0.76</td>
<td>2.39</td>
</tr>
<tr>
<td>CC$_4$</td>
<td>0.62</td>
<td>0.78</td>
<td>2.36</td>
</tr>
<tr>
<td>CC$_6$</td>
<td>0.69</td>
<td>0.81</td>
<td>2.33</td>
</tr>
<tr>
<td>CC$_8$</td>
<td>0.72</td>
<td>0.83</td>
<td>2.31</td>
</tr>
<tr>
<td>CC$_{10}$</td>
<td>0.78</td>
<td>0.86</td>
<td>2.29</td>
</tr>
<tr>
<td>CC$_{20}$</td>
<td>0.89</td>
<td>0.90</td>
<td>2.28</td>
</tr>
</tbody>
</table>

5.5 Discussion

In ZnF$_2$–ZnO–B$_2$O$_3$ glasses or glass ceramics ZnO, generally participate in glass network with ZnO$_4$ structural units and form easily B–O–Zn bridges with BO$_4$ structural units. Such B–O–Zn linkages are more stable than B–O–B and Zn–O–Zn linkages [55, 56]. In addition it is also quite likely that Zn$^{2+}$ ions act as modifiers in the glass network. Earlier structural investigations [57, 58] on some fluoro borate glasses indicated that, in addition to BO$_4$ units, it is rather possible for formation of B(O,F)$_4$ or (BO$_3$F) and BO$_2$F$_2$ units in this type of systems. Cobalt ions are expected to exist mainly in
Co$^{2+}$ state in ZnF$_2$–ZnO–B$_2$O$_3$: CoO glass ceramic network. However, the oxidization of cobalt ions from Co$^{2+}$ to Co$^{3+}$ appears to be possible during melting, annealing and crystallization processes of the glasses. Co$^{2+}$ ions occupy both octahedral and tetrahedral positions, whereas Co$^{3+}$ ions occupy mainly octahedral positions in the glass network [59]. The change of colour of the samples from light blue to thick blue due to crystallization indicated increase of tetrahedral occupancy of the cobalt ions in the glass ceramics [60].

The crystalline phases CoF$_2$ and Co$_3$FB$_7$O$_{13}$ that were detected from the XRD studies indicated that cobalt ions predominantly existed in Co$^{2+}$ state in these glass ceramics. XRD studies also indicated the formation of CoF$_3$, Co$_3$O$_4$, ZnCo$_2$O$_4$ crystallization phases. The presence of such phases confirmed the conversion of a fraction of cobalt ions in to Co$^{3+}$ state in these glass ceramics.

The appearance of multiple crystallization temperatures in the DSC pattern obviously suggested the presence of different phases of crystallization in the samples. We have observed enthalpy (area under the exothermic peaks) to decrease with CoO concentration. This observation indicated the spreading of crystallization from the surface of the sample to the interior portion of the bulk sample gradually [61].

The crystal field splitting of the energy levels of Co$^{2+}$ (d$^7$) ions in tetrahedral field is just similar to d$^3$ electronic configuration in an octahedral
field [62]. The tetrahedral field splits the ground state $^4F$ into $^4A_2$, $^4T_2$ and $^4T_1$ levels, with $^4A_2$ as the lowest. Using Tanabe-Sugano diagrams for the $d^3$ configuration, which is conjugate to $d^7$ ion, the absorption peak observed near to 570 nm was assigned to $^4A_2(^4F) \rightarrow ^4T_1(^4P)$ and the band observed in the NIR region (at about 1390 nm) was assigned to $^4A_2(^4F) \rightarrow ^4T_1(^4F)$. The crystal field parameters ($D_q$, B and C) evaluated for these spectra were furnished in Table 5.4. The negative values of the $D_q$ obtained clearly suggested that Co$^{2+}$ ions were largely located in tetrahedral sites especially in the samples containing high content of CoO. The nephelauxetic ratio, $\beta$ evaluated from the Racah parameter, B, exhibited a decreasing trend. Such tendency suggested the increase of the covalency around Co$^{2+}$ as the concentration of the CoO was increased. In the spectra, we have also observed the shifting of the octahedral band of Co$^{2+}$ ions ($^4T_{1g}(F) \rightarrow ^2T_{1g}(H)$) towards lower wavelength with increase of CoO content; such shift in the position of the bands indicated the decrease in average distance of Co-O. The band identified due to $^5T_2 \rightarrow ^2E$ transition of octahedrally positioned Co$^{3+}$ ions indicated that a part of cobalt ions exists in Co$^{3+}$ state. The increasing intensity and the width of the $^4A_2(^4F) \rightarrow ^4T_1(^4P)$ tetrahedral band suggested a gradual increasing proportion of tetrahedral Co$^{2+}$ ions. We have also observed an increase in the optical band gap with increase in the concentration of crystallizing agent. The tetrahedrally coordinated Co$^{2+}$ ions act as network formers. The higher is the concentration of such network
forming ions the lower is the concentration of non-bridging oxygens in the glass matrix. This led to decrease in the degree of localization of electrons thereby decreased the donor centers in the glass ceramic matrix. The decreasing presence of these donor centers increased the optical band gap and shifted the absorption edge towards lower wavelength side. In other words, the blue-shift of $E_g$ observed with the increase in the content of CoO is associated with increase in the exchange interactions between the $p$ electrons in the conduction band in boron and the localized $d$ electrons of the substitutionally (tetrahedrally) positioned cobalt ions. The fitment of optical absorption spectra, as per the Eqs. 3.1(a) and 3.1(b) indicated that optical band gap was caused by amorphous optical absorption edge as well as indirect band gap (i.e. the transitions in the different points of the Brillouin zone) valid for crystalline materials. This confirmed the fact that the studied materials were formed by direct and partial indirect transitions between the valence band and the conduction band which are valid for amorphous and crystalline materials, respectively.

In the IR spectra, with the gradual increase in the concentration of crystallizing agent CoO, the intensity of BO$_3$ structural units was observed to decrease, whereas that of the bands due to BO$_4$ structural units was observed to increase. Tetragonally positioned Co$_{2+}$ ions do not induce any dangling bonds but octahedrally positioned Co$_{2+}$ ions may do so [63]. The gradual increase in
the intensity of the bands due to BO$_4$ structural units indicated the decreasing presence of cobalt ions in octahedral positions. In addition, the IR spectra of these samples also exhibited two absorption bands at about 620 and 570 cm$^{-1}$. These bands were attributed to the vibrations of Co$^{III}$–O bonds in Co$_3$O$_4$ crystalline phases [42, 64]. Thus this result clearly suggested that in the samples crystallized with CoO, cobalt ions not only existed in Co$^{3+}$ state (in addition to Co$^{2+}$) but also form Co$_3$O$_4$ crystalline phase (as observed in the XRD study) which play crucial role in deciding the insulating strength of the glass ceramics.

The broad and intense emission band observed at about 500 nm in the luminescence spectra of all the glasses including CoO free sample was identified as being due to free-excitons’ recombination in the energy gap. To be more specific this band is due to trapped excitons localized at the ZnO aggregate interface with the glass host [43, 65, 66]. The luminescent transitions for tetrahedral Co$^{2+}$ ions can be determined by the relative locations of $^4T_1(^4P)$ and $^2E(^2G)_1$ excited states. Out of these, the emissions from $^2E$ metastable state are expected to be very narrow set of emission bands, as was reported in number of crystalline and glass ceramic materials [44, 67]. Hence it is justified that in the present case, if we assign the red emission band observed at about 650 nm to $^4T_1(^4P)\rightarrow ^4A_2(^4F)$, whereas NIR band observed at about 870 nm to $^4T_1(^4P)\rightarrow ^4T_2(^4F)$ transition of tetrahedrally positioned Co$^{2+}$ ions, respectively.
The observed increase of PL light output with increase in the content of CoO, supported the viewpoint that there is increasing concentration of tetrahedral Co$^{2+}$ ions in the glass ceramics.

The variation of dielectric constant with the concentration of the nucleating agent, CoO, exhibited maximal effect at $x = 0.2$ mol% (inset of Fig. 5.10). This observation indicated that contribution to dielectric constant due to the space charge polarization is the highest in CC$_2$ glass ceramic owing to the largest degree of disorder in the glass ceramic network. The octahedral cobalt ions act as modifiers and create dangling bonds and non-bridging oxygen ions by disrupting B–O–B and B–O–Zn linkages. Such produced defects create easy pathways for the migration of charge carriers that would enhance the space charge polarization and caused an increase of $\varepsilon'(\omega)$ with temperature [68-70]. The dielectric constant was however, found to be decreased with further increase of CoO content. From the optical absorption, luminescence and IR studies it was evident that with the gradual increase of CoO there is a continuous increase in the concentration of tetrahedral cobalt ions that alternate with BO$_4$ and ZnO$_4$ units and make the glass network more rigid. As a result, there is a blocking of pathways for the migration of charge carriers that would build up space charge. This may account for the observed decrease of dielectric constant with increase of CoO. At higher frequency, $\varepsilon'(\omega)$, for all the studied samples approached a constant value, $\varepsilon'_\infty(\omega)$, which resulted from rapid
polarization processes occurring in the glasses under applied field [71]. At these frequencies the charge carriers would not be able to rotate sufficiently rapidly, so their oscillation would begin to lay behind this field and lead to a decrease of dielectric permittivity, $\varepsilon'(\omega)$.

The variation of dielectric loss, $\tan \delta$ (as well as electric moduli) with frequency and temperature exhibited the relaxation character. The possible dipoles that contribute to the dipolar effects are octahedral complexes of Co$^{2+}$ and Zn$^{2+}$ ions [72]. The increase of activation energy for dipoles and the relaxation time with increase of CoO content (Table 5.6), suggested decreasing degree of freedom for dipoles to orient in the field direction owing to the increase in the rigidity of the glass network with tetrahedral complexes of Co$^{2+}$ ions.

The linear behavior of ac conductivity with activation energy suggested that the conductivity enhancement is directly related to the thermally activated mobility of the charge carriers at higher temperatures. In general, the glass ceramics under study are expected to show mixed, ionic and polaronic, conductivity. The electronic conduction is due to the polaron hopping between Co$^{2+}$ and Co$^{3+}$ ions, whereas the ionic conductivity is due to migration of modifying Zn$^{2+}$ ions. In several fluoride glasses it was also reported that F$^{-}$ ions do contribute to the conductivity [73, 74]. For the studied glasses, the ac conductivity decreased with increasing content of CoO. This behavior can be
explained once again by taking into consideration of gradual increase of tetrahedral Co\textsuperscript{2+} ions in the glass network with increase of CoO content. These tetrahedral cobalt ions act as network formers and decrease the concentration of dangling or floating bonds. This in turn caused an increase in the electrostatic binding energy and the strain energy for the easy migration of charge carriers, which consequently lead to a substantial increment in the jump distance. Such behavior is in good accordance with the observed increase in activation energy for conduction. Therefore, the increase in activation energy and decrease in the conductivity with increasing content of nucleating agent CoO was obviously caused by increasing degree of augmented cross-links in the glass network.

The universal dielectric response (UDR),[75] of the frequency dependent electrical conductivity as mentioned in chapter 4 is general represented by,

\[ \sigma(\omega) = \sigma_{dc} + \omega^n + \omega^s. \]  

(5.1)

The value of exponent \( s \) (obtained by plotting log \( \sigma(\omega) \) vs \( \omega \)) was found to increase with increase of CoO content (Table 5.6). As was pointed out earlier, glasses crystallized with highest concentration of CoO acquired high rigidity because of the tetrahedral participation of cobalt ions. As a result, we expect increase of the Coulomb interaction between mobile ions and decrease of mean free path of the conducting ions. In consequence, there is increase of back-hope rate charger carriers and that lead to increase of \( s \) [76]. In other words, the
larger the concentration of tetrahedral cobalt ions, higher is the concentration of stable ion sites formed in the glass network or lower is the number of conducting pathways; this leads to blocking of efficient zinc ion transport over long distances. In consequence, there is a decrease in the dimensionality for the ion transport in the glass crystallized with higher concentration of CoO.

We have also evaluated density of defect energy states near the Fermi level, \( N(E_F) \), in the nearly temperature independent region of the conductivity (as was described in our earlier chapters) based on the QMT model presented in the Table 5.6. The value of \( N(E_F) \) was found to decrease with increasing concentration of CoO supporting once again supported the view point that there is an increase in the rigidity of the glass network due to decreasing concentration of defect energy states.

The dielectric breakdown strength of \( \text{ZnO–ZnF}_2–\text{B}_2\text{O}_3;\text{CoO} \) glass ceramics measured at room temperature was increased considerably with increase of CoO concentration indicating increase of insulating strength of the studied glass ceramic with increase of CoO content. The value of breakdown strength was found to be in the range of 12.9 to 19.2 kV/cm. such value of breakdown strength is still far greater than the required value for a material to be used as dielectric layer in PDP’s [77].
5.6 Conclusions

ZnO−ZnF₂−B₂O₃ glasses were crystallized with different concentrations of CoO. The scanning electron microscopic studies indicated that the samples contain well defined and randomly distributed crystal grains. The X-ray diffraction studies indicated the formation of Co²⁺ and Co³⁺ crystalline phases. The study of DSC suggested the crystallization spreads from surface to the interior of the samples as the concentration of CoO is increased. The IR spectral studies pointed out that there is a decreasing degree of depolymerization of the glass network with increase of CoO content. The optical absorption and photoluminescence spectra of ZnO−ZnF₂−B₂O₃:CoO glass ceramics exhibited bands due to tetragonal and octahedral transitions of Co²⁺ ions. In addition the traces of Co³⁺ ions could also be located from these studies. As the concentration CoO was increased the tetrahedral transitions of Co²⁺ prevailed over the octahedral transitions. The analysis of the results of dielectric studies suggested increase in the insulating character of these samples with increase in the concentration of crystallizing agent. The room temperature dielectric constant of these glass ceramics was found to be in the range of 15−16.4 and the breakdown strength is > 10.5 kV/cm suggesting that ZnO−ZnF₂−B₂O₃ glasses crystallized with larger concentration CoO would be suitable for dielectric layer in plasma display panels.
Reference


