PREFACE

The present thesis deals with the studies on “Dielectric and Spectroscopic investigations on some transition metal ions doped ZnO–ZnF$_2$–B$_2$O$_3$ glass ceramics”. This work has been carried out in the Department of Physics, Acharya Nagarjuna University, Nagarjuna Nagar. The thesis contains the methods of preparation, characterization and studies on dielectric and spectroscopic properties of ZnO–ZnF$_2$–B$_2$O$_3$ glass systems crystallized with varying concentration of TiO$_2$, MoO$_3$ and CoO.

Among different glass systems ZnO mixed borate or silicate glasses possess 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. Zinc oxide based glasses are being widely used in plasma display panels in large area hang-on-wall TVs and computer monitors for high quality and performance. In plasma display panels, a dielectric layer is formed on the glass substrate so as to cover the display electrodes. It is necessary for the dielectric layer to maintain discharge, to have a high dielectric strength and to have good transparency, high dielectric break down voltage. ZnO based glass material meet these requirements. 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.

Glass ceramic materials doped by transition metal ions are expected to be promising candidates as gain media for ultra-broadband optical fiber amplifiers, tunable lasers and ultra short pulse lasers in telecommunication wavelength regions over the glass materials. This is because of the dominance of non-radiative losses over the relaxations of excited states of transition metal ions/lasing spices in these materials and they increase the dielectric breakdown strength of the glasses. The glass ceramic materials possess a fine-grained uniform structure, consisting of small crystals of irregular and distorted form, often aggregated into spherolites, with residual glass inter-layers cementing the crystalline glass ceramic cluster. These small and strain free intertwined microcrystals hinder the crack growth inside these materials. As a result, glass ceramics are likely to have outstanding mechanical, optical, electrical and thermal characteristics.

Among various crystallizing agents, TiO$_2$ is expected to be more effective mineralizer especially in the glass systems like ZnO–ZnF$_2$–B$_2$O$_3$ when compared with the other nucleating agents. In general, the ions of titanium exist in the glass in Ti$^{4+}$ state and participate in the glass network forming with different principal polyhedral, viz., TiO$_4$, TiO$_6$ and sometimes with TiO$_5$ (comprising of trigonal bipyramids) structural units. The inclusion of Ti$^{4+}$ ions into this glass is an
advantage since the empty or unfilled 3d–shells of Ti ions contribute substantially to the non–linear second-order polarizabilities described by the third rank polar tensors. This one allows to produce multi-functional elements for quantum electronics with these glasses. Titanium ions may also exist in Ti$^{3+}$ valence state in glass matrices and expected to influence the physical properties of the glass to a large extent.

Similarly another interesting transition metal oxide MoO$_3$ is expected to be more effective mineralizer especially in the glass systems like zinc oxy borate glass systems. Molybdenum oxide has already been used successfully as crystallization catalyst in a number of other glass systems. Further, these ions are expected to have profound influence on the optical and electrochemical properties of ZnO–B$_2$O$_3$ glass ceramics in view of the fact that the oxide of molybdenum participate in the glass network with different structural units like MoO$_4$ (T$_d$) and MoO$_6$ (O$_h$) of Mo$^{6+}$ ions and Mo$^{5+}$O$^{3-}$ (O$_h$) of Mo$^{5+}$ ions. The presence of molybdenum ions further makes the glasses to be useful for potential applications in high-density memories, light modulation, large area displays devices like smart windows and other electro-chromic devices.

Likewise, another interesting transition metal ion viz., cobalt ions exist in two stable valence states, viz., Co$^{2+}$ and Co$^{3+}$. Co$^{2+}$ ions participate in the glass network in octahedral and tetrahedral co-ordinations. The concentration of CoO$_4$ and 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.

Thus the clear objectives of the present study are to prepare, characterize and

- To have a comprehensive understanding over the influence of titanium ions on structural aspects and insulating strength of ZnO–ZnF₂–B₂O₃ glass ceramics by investigating the dielectric properties, optical absorption and IR, luminescence spectra and photoinduced second order susceptibility.

- To have a broad perceptive over the role of molybdenum ions on the structural aspects of ZnO–ZnF₂–B₂O₃ glass ceramic system from a systematic study of various dielectric properties coupled with spectroscopic studies and throw light on influence of molybdenum ions on the electrical breakdown strength of the glass ceramic.

- To study dielectric properties (over a long range of frequency and temperature) and dielectric breakdown strength of ZnO–ZnF₂–B₂O₃:CoO glass ceramics to estimate the change in its insulating strength and to identify the 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.

The compositions of the glasses used for the present study are

1. (10-x) ZnO–30ZnF₂–60B₂O₃: x TiO₂ (0 ≤ x ≤ 0.5)
2. (10-x) ZnO–30ZnF₂–60B₂O₃: x MoO₃ (0 ≤ x ≤ 1.0)
3. (10-x) ZnO–30ZnF₂–60B₂O₃: x CoO (0 ≤ x ≤ 2.0)
The glasses were prepared by the usual melting, quenching and subsequent annealing techniques. Later the samples were crystallized by heating them at crystallization temperature (identified from DSC scans of the amorphous materials) for prolonged times. The samples were characterized by X-ray diffraction, scanning electron microscopy, EDS and differential scanning calorimetric techniques.

The following measurements were taken:

1) Dielectric constant ($\varepsilon'$), loss ($\tan \delta$) and ac conductivity $\sigma_{ac}$ in frequency range $10^2$–$10^6$ Hz and in the temperature range 30-300 °C.

2) Optical absorption in the UV, visible and NIR regions at room temperature.

3) Infrared spectra of transition all glass ceramic samples in the region 400 to 4000 cm$^{-1}$.

4) Photoluminescence spectra in the visible regions at room temperature of MoO$_3$ and CoO doped glass ceramics.

5) Electron spin resonance spectra at room temperature for MoO$_3$ doped glass ceramics samples.

For the sake of convenience, the thesis is divided into six chapters.

CHAPTER–I presents the General Introduction, Scope, Contents and the Aim of the present work. In this chapter, the basic theory related to electrical
and spectroscopic properties of ZnO–ZnF₂–B₂O₃: TiO₂/MoO₃/CoO glass ceramics.

**CHAPTER–II** gives the description of experimental methods employed in the preparation and characterization of ZnO–ZnF₂–B₂O₃: TiO₂/MoO₃/CoO glass ceramics. The samples were crystallized by heating the glass samples for 72 h at the crystallization temperature identified from the DSC studies. The details of the apparatus used and the techniques adopted for characterization and for measuring dielectric properties, optical absorption, ESR, IR and photoluminescence are also described in detail in this chapter.

The scanning electron microscopic (SEM) pictures of the pre-heated samples containing different concentration of transition metal oxides did not show any significant crystallinity. The pictures of the crystallized ZnO–ZnF₂–B₂O₃ glasses with different concentrations nucleating agents exhibited well defined and randomly distributed crystals entrenched in glassy matrix.

The differential scanning calorimetric (DSC) of all the crystallized samples exhibited endothermic change due to the glass transition followed by multiple exothermic effects due to the crystal growth indicating the presence of different crystalline phases in the samples. The DSC data could further be explained in terms of surface and bulk crystallization in all the series of the samples.

In **CHAPTER-III** the results of investigations on dielectric properties and spectroscopic properties (optical absorption, IR) of ZnO–ZnF₂–B₂O₃ glasses
crystallized with different concentrations of TiO₂ have been presented and were discussed in the light of principal role of the titanium valence states and its coordination number in the glass ceramics.

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

TC₀: 10.0ZnO–30ZnF₂–60B₂O₃
TC₁: 9.9ZnO–30ZnF₂–60B₂O₃: 0.1TiO₂
TC₂: 9.8ZnO–30ZnF₂–60B₂O₃: 0.2TiO₂
TC₃: 9.7ZnO–30ZnF₂–60B₂O₃: 0.3TiO₂
TC₄: 9.6ZnO–30ZnF₂–60B₂O₃: 0.4TiO₂
TC₅: 9.5ZnO–30ZnF₂–60B₂O₃: 0.5TiO₂

The X-ray diffraction pattern of TiO₂ mixed glass ceramic samples exhibited peaks due to αZn(BO₂)₂, ZnTiO₅, ZnO, Zn₂TiO₄, TiF₃ and TiOF₂; crystal phases. The presence of TiF₃ crystal phases pointed out that there is a possibility for the titanium ions to exist in Ti³⁺ state, whereas, rest of the phases indicated that these ions existed in Ti⁴⁺ state.

The Infrared transmission spectra of TiO₂ free ZnO–ZnF₂–B₂O₃ glass ceramic exhibited two groups of bands: (i) in the region 1200 – 1600 cm⁻¹, (ii) in the region 800–1200 cm⁻¹ and another band at about 690 cm⁻¹. The second group of bands was attributed to the BO₄ units while the first group of bands was identified as being due to the stretching relaxation of the B–O bond of the trigonal BO₃ units and the band at 670 cm⁻¹ is due to the bending vibrations of B–O–B linkages in the borate network. Additionally, a band at about 488 cm⁻¹
was also observed in the spectra of all the glasses; this band was attributed to the vibrations of ZnO$_4$ tetrahedral units.

The spectra of the samples crystallized with TiO$_2$ exhibited two new bands in the regions 710–750 cm$^{-1}$ and 625–640 cm$^{-1}$. These bands were identified as originated from Ti–O–Ti symmetric stretching vibrations of TiO$_4$ (tetrahedral) and due to the vibrations of TiO$_6$ (octahedral) units, respectively. As the concentration of TiO$_2$ was increased, the band due TiO$_6$ (octahedral) grown gradually at the expense of TiO$_4$ tetrahedral band. In addition, with increase in the concentration of TiO$_2$, intensity of band due to BO$_3$ structural units is observed to increase at the expense of band due to BO$_4$ structural units. From this observation it was concluded that as the concentration of the TiO$_2$ is increased there was a gradual increase in the degree of disorder in the glass ceramic.

The optical absorption spectra of ZnO–ZnF$_2$–B$_2$O$_3$:TiO$_2$ glass ceramics exhibited two weak absorption bands at about 517 and 686 nm. The observed bands were identified as being due to $^2$B$_{2g}$$\rightarrow$$^2$B$_{1g}$ and $^2$B$_{2g}$$\rightarrow$$^2$A$_{1g}$ octahedral transitions of the Ti$^{3+}$ (d$^1$) ions, respectively. As the concentration of TiO$_2$ was increased, the half width and intensity of these two bands were observed to increase. Such increase was attributed to the increasing fraction of Ti$^{4+}$ ions that have been reduced in to Ti$^{3+}$ ions. The analysis of results of optical band gap of these samples indicated that the studied materials were formed by direct and partial indirect transitions between the valence band and the conduction band.
The variations of dielectric properties (viz., dielectric constant, \( \varepsilon'(\omega) \), and loss, \( \tan \delta \)) with temperature of ZnO–ZnF\(_2\)–B\(_2\)O\(_3\):TiO\(_2\) glass ceramics have been analyzed on the basis of different polarizations. The frequency and temperature dependence of the dielectric loss parameters have exhibited relaxation character. The relaxation effects have been attributed to complexes of Zn\(^{2+}\) and Ti\(^{3+}\) ions. The observed increase in the electrical conductivity and decrease in the activation energy with increase in the concentration of the crystallizing agent (TiO\(_2\)) is attributed to two effects. One is due to the contribution of polaron Ti\(^{3+}\)–Ti\(^{4+}\) pairs and the other is related to the significant ionic contribution due to an increase in the concentration of dangling bonds which leads to the substantial decrement in jump distance for zinc ions. The dielectric breakdown strength of these glass ceramics was found to decrease with increase of TiO\(_2\) concentration.

The objective of the \textbf{CHAPTER-IV} is to synthesize ZnO–ZnF\(_2\)–B\(_2\)O\(_3\) glass ceramics with different concentrations of MoO\(_3\) as nucleating agent, to characterize by variety of techniques viz., XRD, SEM, DSC. The studies taken up are dielectric properties, dielectric breakdown strength and spectroscopic properties (optical absorption, ESR, IR and photoluminescence).

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

CM\(_2\): 9.8ZnO–30ZnF\(_2\)–60B\(_2\)O\(_3\): 0.2MoO\(_3\)
CM\(_4\): 9.6ZnO–30ZnF\(_2\)–60B\(_2\)O\(_3\): 0.4MoO\(_3\)
CM\(_6\): 9.4ZnO–30ZnF\(_2\)–60B\(_2\)O\(_3\): 0.6MoO\(_3\)
CM₈: 9.2ZnO–30ZnF₂–60B₂O₃: 0.8MoO₃
CM₁₀: 9.0ZnO–30ZnF₂–60B₂O₃: 1.0MoO₃

The X-ray diffraction studies of MoO₃ mixed glass ceramic samples exhibited peaks due to αZn(BO₂)₂, Zn₃Mo₂O₉, ZnMoF₇, (Zn)₃(BO₃)₂ and ZnMoO₄ crystalline phases. The presence of diffraction peaks due to Zn₃Mo₂O₉ (at 2θ = 21.21°, 34.08°, 51.20°) and ZnMoO₄ (at 2θ = 53.77°) indicated majority of molybdenum ions existed in Mo⁶⁺ state. As the concentration of MoO₃ was increased, the intensity of these peaks was found to decrease while a new diffraction peak appeared due to ZnMoF₇ crystal phase (an Mo⁵⁺ crystal phase) at about 2θ = 23.42°. The intensity of this particular peak was found to increase gradually with increasing of MoO₃ content.

The IR spectra of MoO₃ doped samples exhibited two new bands in the regions 900–925 cm⁻¹ and 800–820 cm⁻¹ due to ν₁ and ν₃ vibrational modes of MoO₄²⁻ tetrahedral units, respectively. With increase in the concentration of crystallizing agent MoO₃, the intensity of band due to ν₁ – MoO₄²⁻ vibrations was observed to decrease and found to be shifted towards slightly higher wavenumber, whereas, the ν₃ vibrational band of these units exhibit a shift towards lower wavenumber. Further, intensity of band due to BO₃ structural units was observed to increase at the expense of band due to BO₄ structural units with increase of MoO₃ content. The analysis these results indicated that there is an increase of de-polymerization of the glass ceramic network with increase of MoO₃ content.
The optical absorption spectra of MoO$_3$ doped glass ceramics recorded at room temperature exhibited a broad absorption band with meta-center at about 710 nm. This band was predicted due to the $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xz-yz}$ excitation of Mo$^{5+}$ ($4d^1$) ion. The inter charge transition transfer (viz. Mo$^{5+} \leftrightarrow$ Mo$^{6+}$) in the glass network prevented the resolution of these two transitions. The highest intensity of this band observed in the spectrum of sample CM$_{10}$ indicated the presence of higher concentration of Mo$^{5+}$ ions in this glass ceramic. Such Mo$^{5+}$ ions might form (Mo$^{5+}$O$_3$)$^-$ molecular orbital states and were expected to participate in the depolymerization of the glass network.

ESR and photoluminescence spectra of MoO$_3$ doped glass ceramics have revealed that the there is an increasing proportion Mo$^{5+}$ ions with increase in the concentration of MoO$_3$ in the glass ceramic. These Mo$^{5+}$ ions were found to form molybdenyl complexes with non-bridging oxygens and act as modifiers. The presence of higher concentration of Mo$^{5+}$ ions was found to be a hindrance for making the material suitable for light emission in the blue, green and red region.

The variations of dielectric constant, $\varepsilon'(\omega)$, and loss, tan $\delta$, with temperature of MoO$_3$ doped glass ceramics have been analyzed using different types of dielectric polarizations. The frequency and temperature dependence of the dielectric loss and electric moduli parameters have exhibited relaxation character. The relaxation effects have been attributed to molybdenyl complexes in addition to Zn$^{2+}$ and. The observed increase in the electrical conductivity and decrease in the activation energy with increase in the concentration of the
crystallizing agent (MoO$_3$) is attributed (i) to the contribution of polaronic transfer between Mo$^{5+}$↔Mo$^{6+}$ ions and (ii) due to the significant ionic contribution because of increase in the concentration of dangling bonds that facilitate to the substantial decrement in jump distance for zinc ions between the two sites in the ceramic network. The room temperature dielectric constant of these glass ceramics containing even the highest concentration of MoO$_3$ is always found to be in between 11.5 and 12.4 and the breakdown strength is $>10.5$ kV/cm suggesting that these glass ceramics would be suitable for dielectric layer in PDPs at room temperature. If the care is taken to minimize Mo$^{5+}$ ion concentration these glass ceramics, the transparency can also be increased in visible region and makes the material more useful for PDP panels.

**CHAPTER-V** is devoted to the studies on CoO doped ZnO–ZnF$_2$–B$_2$O$_3$ glass ceramics. The detailed compositions of the glasses used in this investigation were as follows:

- **CC$_2$**: 9.8ZnO–30ZnF$_2$–60B$_2$O$_3$: 0.2CoO
- **CC$_4$**: 9.6ZnO–30ZnF$_2$–60B$_2$O$_3$: 0.4 CoO
- **CC$_6$**: 9.4ZnO–30ZnF$_2$–60B$_2$O$_3$: 0.6 CoO
- **CC$_8$**: 9.2ZnO–30ZnF$_2$–60B$_2$O$_3$: 0.8 CoO
- **CC$_{10}$**: 9.0ZnO–30ZnF$_2$–60B$_2$O$_3$: 1.0 CoO
- **CC$_{20}$**: 8.0ZnO–30ZnF$_2$–60B$_2$O$_3$: 2.0 CoO

The X-ray diffraction studies of these glass ceramics exhibited diffraction peaks due to αZn(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$_4$
crystal phases. The presence of diffraction peaks due to CoF$_2$ and Co$_3$FB$_7$O$_{13}$ crystal phases at $2\theta=26.62^\circ$ 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$_3$ ($2\theta = 28.55^\circ$, $39.79^\circ$) and ZnCo$_2$O$_4$ ($2\theta = 31.21^\circ$, $36.85^\circ$) crystalline phases indicated that a part of cobalt ions existed in Co$^{3+}$ state.

The IR spectra of CoO doped samples exhibited two weak kinks, identified as being due to the vibrations of Co$^{III} - O$ were also located in these spectra in the region 540–600 cm$^{-1}$. As the concentration of CoO was increased, the vibrational band due to BO$_4$ structural units was observed to grow at the expense of band due to BO$_3$ units. Additionally, the BO$_4$ band exhibited a considerable shift towards lower wavenumber. From these results, it was concluded that there was an increase of polymerization of the glass ceramic with increase of CoO content.

The optical absorption spectra of CoO mixed glass ceramics exhibited three principal absorption bands at 530 nm, 563 nm and at about 1378 nm. Out of these, the band at 530 nm was identified as being due to $T_{1g}(F)\rightarrow^2T_{1g}(H)$ octahedral transition, whereas the latter bands were attributed to $^4A_2(^4F)\rightarrow^4T_1(^4P)$ and $^4A_2(^4F)\rightarrow^4T_1(^4F)$ tetrahedral transitions of Co$^{2+}$ ions, respectively. The spectra also exhibited an additional kink at about 669 nm and this was predicted due to $^5T_{2g}\rightarrow^5E_g$ octahedral transition of Co$^{3+}$ ions. 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. From these observations it was concluded that when CoO was present in higher concentrations Co$^{2+}$ ions predominantly occupied tetrahedral positions and decreased the degree of disorder in the glass ceramic network.

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 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 three series of glass ceramics. This band was envisaged due to free-excitons’ recombination in the energy gap. The remaining two emission bands in the regions 600–700 nm and 800–900 nm were identified as being due to $^{4}T_1(^4P) \rightarrow ^{4}A_2(^4F)$ and $^{4}T_1(^4F) \rightarrow ^{4}A_2(^4F)$ tetrahedral transitions of Co$^{2+}$ ion, respectively. 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. The observed increase of PL light output with increase in the content of CoO, supported the view point that there is increasing concentration of tetrahedral Co$^{2+}$ ions in the glass ceramics.

The analysis of the results of dielectric studies of CoO doped samples has 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.

CHAPTER-VI reports brief summary and conclusions drawn from the investigation carried out on a variety of properties viz., (a) dielectric, and (b) spectroscopic properties of ZnO–ZnF₂–B₂O₃ glass systems crystallized with varying concentration of TiO₂, MoO₃ and CoO.

References closely related to the present work have been compiled to the extent possible and given at the end of the relevant chapter.