PREFACE

The present work concerns with “Non-linear optical, piezoelectric, elastic, spectroscopic and dielectric studies on ZnF$_2$–PbO–TeO$_2$: TiO$_2$ glass ceramics” This work has been carried out in the Department of Physics, Acharya Nagarjuna University – Nuzvid Campus, Nuzvid. The thesis contains the methods of preparation, characterization and studies on non-linear optical properties, piezoelectric, elastic properties, dielectric properties and spectroscopic properties (viz., optical absorption, infrared, Raman, and ESR) of ZnF$_2$–PbO–TeO$_2$ glasses crystallized with different concentrations of TiO$_2$.

Among various glass systems tellurium oxide based glasses are the subject of intense current research because of their interesting non-linear, electrical and optical properties. Compared with silicate and borate glasses, tellurite glasses have several superior physical properties such as high dielectric constant, high refractive index, large non-linear optical susceptibility, good chemical resistance and good infrared transmissivity.

In view of these qualities, tellurite based glasses were considered as potential candidates as nonlinear optical materials, as the best materials for optical components such as IR domes, optical filters, modulators, memories and laser windows.
Photoinduced study on these glasses has been the subject of high interest in recent years due to their potential applications mentioned above. The understanding of the origin of optical susceptibilities in tellurite glasses and the corresponding glass ceramics stimulated by ultra-short laser pulses has gained momentum in the recent years. Such studies in fact help in examining the suitability of the materials for potential applications like three-dimensional photonic devices for integrated optics and other laser-operated devices (such as ultrafast optical switches, optical fiber modulators, power limiters, broad band optical amplifiers).

The origin of these properties has been strongly correlated to the local order around tellurium atoms. The coordination geometry of Te atoms has been shown to be strongly dependent on the composition of the glasses and on the chemical nature of the glassy network modifier. For example, the addition of transition metal oxides to the TeO$_2$ matrix, changes the coordination of Te from a TeO$_4$ trigonal bipyramid (tbp) group to a TeO$_3$ trigonal pyramid (tp) through intermediate polyhedra TeO$_{3+1}$. The TeO$_4$ tbp group has two axial and two equatorial oxygen atoms, in which an electron pair occupies the third equatorial position of the sp$^3$d hybrid orbital. The presence of this electron pair plays a key role in the structure building and manifestation of non-linear optical properties of tellurite glasses.
We have chosen ZnF$_2$–PbO–TeO$_2$ glass system for the present study. Addition of the modifier like ZnF$_2$ to PbO–TeO$_2$ glass matrix is expected to lower the viscosity and to decrease the liquidus temperature to a substantial extent and makes the glass more moisture resistant and also acts as effective mineralizer.

PbO may act as modifier and facilitate glass formation of TeO$_2$, since TeO$_2$ as such is an incipient glass former. PbO may also act as glass network former and participate in the glass network with [PbO$_{4/2}$] pyramidal units connected in puckered layers. Additionally, earlier it was reported that PbO also plays a crucial role in inducing the non-polar effects in the glass materials because of its high electrical polarizability. TiO$_2$ is chosen as the crystallizing agent because it is quite likely that the titanium ions do form interesting tetragonal ferroelectric crystalline phases like Pb$_5$Ti$_3$F$_{19}$, PbTiO$_3$ and PbTeO$_3$ in these samples which contribute to second order non-linear optical coefficients, piezoelectric coefficient ($d_{33}$) substantially.

Though considerable studies on electrical properties along with optical properties of some TeO$_2$ based glasses are available in literature, majority of these studies are devoted to binary tellurite glasses and further they are mainly concentrated on dc conductivity studies. Much devoted studies on non-linear optical properties, piezoelectric properties, elastic properties, dielectric relaxation and ac conductivity of ZnF$_2$–PbO–TeO$_2$ glasses crystallized with transition metal oxides like TiO$_2$ are very rare. Knowledge on these properties
is highly helpful for assessing the suitability of these materials for non-linear optical devices.

Among various transition metal oxides, TiO$_2$ is expected to be more effective mineralizer especially in the glass systems like tellurite exhibiting high optical susceptibilities. Normally, the ions of titanium, exist in the glass in Ti$^{4+}$ state and participate in the glass network forming with different principal polyhedral: TiO$_4$, TiO$_6$ and some times with TiO$_5$ (comprising of trigonal bipyramids) structural units. However, there are reports suggesting that these ions may also exist in Ti$^{3+}$ valence state in some of the glass matrices. Further the inclusion of Ti$^{4+}$ ions into the tellurite glass ceramic network is substantial advantage to use these materials for optically operated devices, since the empty or unfilled 3d-shells of Ti ions contribute more strongly to the non-linear polarizabilities that can be determined prevailingly by optical/electrical Kerr effect.

In view of these, it is felt worthwhile to have some understanding over the dielectric, dc field and photoinduced second order susceptibilities, piezoelectric, elastic and spectroscopic properties of ZnF$_2$–PbO–TeO$_2$ glasses crystallized with TiO$_2$. The studies on photoinduced second order susceptibilities coupled with spectroscopic (viz., optical absorption, electron spin resonance, infrared and Raman spectra) help to assess the suitability of these materials for NLO devices, the study on piezoelectric properties will help
in examining the aptness of these glass ceramics in the design of miniature sensors and actuators, study on elastic properties will help in estimating the mechanical strength, whereas the studies on dielectric properties give the information on insulating strength of these materials and also help in understanding the structural aspects.

Thus the clear objectives of the present study are

- To synthesize ZnF₂–PbO–TeO₂ glasses, crystallize them with different concentrations of TiO₂ as nucleating agent and characterize them by variety of techniques viz., XRD, SEM, TEM and DSC.

- To study optical absorption, ESR, IR and Raman spectra to have some pre-assessment over the structural aspects of the titled glass ceramics.

- To study second order susceptibility (after the samples were dc field poled at elevated temperatures), photo-induced changes (change in the refractive index with the probe wavelength) and to discuss the correlation between glass structure and non-linear optical (NLO) susceptibilities.

- To study the piezoelectric coefficients coupled with elastic properties as a function of the concentration of crystallizing agent and to analyze the results within a framework of different crystal phases formed in the glass ceramics.
To investigate dielectric dispersion behavior over a frequency range of $10^{-2}$ to $10^6$ Hz and within the temperature range 303 to 523 K and to obtain some information on insulating character of these glass ceramics.

The compositions of the samples used in the present study are:

$$30\text{ZnF}_2-(10.0-x)\text{ PbO} - 60\text{TeO}_2: x \text{ TiO}_2 \ (0 \leq x \leq 2.0), \text{ all in wt\%}$$

The studies carried out are

(i) differential scanning calorimetry in the temperature range 303–1500 K and the evaluation of glass transition temperature, $T_g$, crystallization temperature, $T_C$.

(ii) infrared spectra (in the range 400–2000 cm$^{-1}$) and Raman spectra (in the range 300–1500 cm$^{-1}$) and to identify various structural units present in the samples.

(iii) optical absorption studies in the wavelength range 300–900 nm and identification of electronic transitions of titanium ions.

(iv) electron spin resonance measurements and the identification of the positions and valence states of titanium ions in the glass network.

(v) second order optical susceptibility as a function of the concentration of crystallizing agent TiO$_2$ by recording the power of the output spectrally separated second-harmonic wave generated (SHG) intensity for the dc-poled (4 kV/cm and at 400 °C) samples.
(vi) the non-linear optical effects (change in refractive index) as a function of wavelength after the achievement of maximal sample’s polarization by applying electrostatic strength 4 kV/cm with simultaneous heating of the sample up to 400°C and to discuss the correlation between glass structure and non-linear optical (NLO) susceptibilities.

(vii) variation of piezoelectric coefficient $d_{33}$ with the concentration of nucleating agent TiO$_2$ at room temperature and to analyze the results within a framework of different crystal phases formed in the glass ceramics.

(viii) ultrasonic velocity in the samples at room temperature by echo pulse technique (PE) and to estimate different elastic coefficients and acoustic parameters and to have some information over the mechanical strength of the samples.

(ix) dielectric properties viz., dielectric constant $\varepsilon_r$, dielectric loss tan $\delta$ and ac conductivity $\sigma_{ac}$ in the frequency range $10^{-2}$–$10^6$ Hz and in the temperature range 303–523 K and also dc conductivity and to analyze the results in the light of different polarization and conduction mechanisms.

For the sake of convenience the thesis is divided into seven chapters.
\textbf{Chapter–I} presents the General Introduction, Scope, Contents and the Aim of the present work. In this chapter, the basic theory related to dielectric, spectroscopic properties and brief introduction on non-linear optical properties, piezoelectric properties and elastic properties of ZnF$_2$–PbO–TeO$_2$ glasses crystallized with different concentrations of TiO$_2$ is presented systematically.

In \textbf{Chapter–II} the detailed description of the methods used in the preparation of glasses and glass ceramics and the results of characterization of the ZnF$_2$–PbO–TeO$_2$: TiO$_2$ glass ceramics are presented. The methods include X-Ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), differential scanning calorimetry (DSC). $30\text{ZnF}_2-(10.0-x)\text{PbO– 60TeO}_2$: $x\text{TiO}_2$ $(0 \leq x \leq 2.0)$, all in wt\%. The glasses were prepared by the usual melting, quenching and subsequent annealing techniques. Later the samples were crystallized at the temperature corresponding to the crystallization temperature identified from the DSC patterns.

The X-ray diffraction studies have indicated that the crystallized samples contain variety of crystal phases; some of them are Pb$_5$Ti$_3$F$_{19}$, PbTiO$_3$, PbTi$_2$O$_6$, PbTeO$_3$, Pb$_3$TeO$_5$, and TiTe$_2$O$_8$. These studies have also indicated the concentration of Pb$_5$Ti$_3$F$_{19}$ crystal grains (in which titanium ions exist in Ti$^{3+}$ state) is the highest in the samples crystallized with 1.0 wt\% of TiO$_2$. The scanning electron microscopic (SEM) and transmission electron microscopy
(TEM) pictures of the pre-heated samples containing different concentration of TiO$_2$ do not show any significant crystallinity. The pictures of the heat treated of ZnF$_2$–PbO–TeO$_2$ glasses with different concentrations of nucleating agent (TiO$_2$) indicated that well defined, randomly distributed crystals of different sizes (varying from 50 to 500 nm) were ingrain in glassy matrix. The differential scanning calorimetric (DSC) scans in the temperature region 300-1500 K of ZnF$_2$–PbO–TeO$_2$:TiO$_2$ glass ceramics exhibited a weak endothermic effect (due to glass transition) in the temperature range 590 to 610 K. At about 770 K, the DSC thermograms of each glass ceramic sample exhibited well-defined exothermic effects with multiple steps of crystallization temperatures. From these results it is concluded that the samples contain different crystalline phases. The thermal gravimetric analysis of these samples indicated virtually no change in the mass of the samples upto 1100 K.

**Chapter III** is devoted to present the results on studies of different spectroscopic studies of ZnF$_2$–PbO–TeO$_2$ : TiO$_2$ glass ceramics with a view to explore the influence of titanium valance states and their coordination with oxygen on structural and optoelectronic aspects of the samples. The studies undertaken are infrared (IR), Raman, optical absorption and ESR spectra. The infrared spectra of ZnF$_2$–PbO–TeO$_2$:TiO$_2$ glass ceramics exhibited the bands at 460 cm$^{-1}$ (due to PbO$_4$ units), 650–700 cm$^{-1}$ (due to TeO$_2$ axial $v_2$(A$_2$)–$v$'$_{TeO_{ax}}$/TiO$_6$ structural units), 750–800 cm$^{-1}$ (due to TeO$_2$ equatorial $v$(A$_1$) –
As the concentration of TiO\textsubscript{2} is increased up to 1.0 wt\%, the band due to ν\textsubscript{TeO\textsubscript{eq}}/TiO\textsubscript{6} structural units is observed to grow gradually and shifts towards lower energies. A slight reversal trend in the intensity of this band could be visualized when the concentration of TiO\textsubscript{2} is raised beyond 1.0 wt\%.

Raman spectra of ZnF\textsubscript{2}–PbO–TeO\textsubscript{2}: TiO\textsubscript{2} glass ceramics exhibited spectral bands due to the stretching vibrations of Te–O–Te linkages between TeO\textsubscript{4} trigonal bipyramids (tbp), Te–O stretching vibrations of TeO\textsubscript{4} tbp units, [TeO\textsubscript{3+1}]\textsuperscript{4−} and [TeO\textsubscript{3}]\textsuperscript{2−} units. The spectra also exhibited bands due to TiO\textsubscript{4} structural units and asymmetric TiO\textsubscript{5} entities. With increasing TiO\textsubscript{2} content, the intensity of the bands due to TeO\textsubscript{4} bipyramids and TiO\textsubscript{4} structural units are decreased, whereas that of the bands due to [TeO\textsubscript{3+1}]\textsuperscript{4−}, [TeO\textsubscript{3}]\textsuperscript{2−} and TiO\textsubscript{5} units are enhanced and exhibited maximum intensity at 1.0 wt\% of TiO\textsubscript{2}.

The analysis of these results has indicated that the titanium ions present largely in octahedral positions in the sample TC\textsubscript{10} and titanium ions predominantly act as modifiers.

The optical absorption spectra of ZnF\textsubscript{2}–PbO–TeO\textsubscript{2}: TiO\textsubscript{2} glass ceramic samples exhibited two clearly resolved absorption bands in the spectral range 550–560 and 660–680 nm assigned to \(2\text{B}_{2g} \rightarrow 2\text{B}_{1g}\) and \(2\text{B}_{2g} \rightarrow 2\text{E}_{1g}\) transitions of the Ti\textsuperscript{3+} (3d\textsuperscript{1}) ion, respectively. As the concentration of TiO\textsubscript{2} is continued to increase up to 1.0 wt\% the half width and intensity of these two bands are
observed to increase with a slight shift in the peak positions towards higher wavelength. From these results it is concluded that there is a higher fraction of Ti$^{4+}$ ions that have been reduced in to Ti$^{3+}$ ions in the glass sample crystallized with 1.0 wt% of TiO$_2$. ESR spectra of ZnF$_2$–PbO–TeO$_2$:TiO$_2$ glass ceramic samples recorded at room temperature exhibited and intense asymmetric spectral line centered at about $g = 1.9485$ due to Ti$^{3+}$ ($3d^1$) ion. The half width and the intensity of this signal has exhibited maximal effects at the concentrations at $x = 1.0$ wt%. The analysis of these results indicated that the fraction of Ti$^{3+}$ is the highest in the sample TC$_{10}$.

In Chapter IV we have included the results on second order susceptibility studies (after the samples were dc field poled at elevated temperatures), photo-induced changes (variations in the refractive index with the probe wavelength) and discussed the correlation between glass ceramic structure and the obtained non-linear optical (NLO) susceptibilities.

The second-order optical susceptibility ($\chi^{(2)}$) of ZnF$_2$–PbO–TeO$_2$: TiO$_2$ glass ceramic samples is found to increase with the concentration of TiO$_2$ content up to 1.0 wt%. When the concentration of TiO$_2$ is increased from 1.0 to 1.5 wt%, a considerable decrease of $\chi^{(2)}$ is observed. For further rise of TiO$_2$ content the value of susceptibility is observed to increase. Electrically-induced birefringence ($\Delta n$–change in refractive index) with the probe wavelength for the glass ceramics is observed to decrease with increase in probe wavelength
and exhibited an upward kink at about 570 nm for the samples containing any concentration of TiO$_2$. Further, we have identified that the variation of $\Delta n$ with the concentration of TiO$_2$ is similar to that of second order susceptibility.

The analysis of the results indicated that Pb$_5$Ti$_3$F$_{19}$ crystal phases are the main contributors to the non-linear optical (NLO) effects and higher concentration of such phases are found to be responsible for the maximal effects of $\chi^{(2)}$ and $\Delta n$ at $x = 1.0$ wt%. Additionally, PbTiO$_3$ and PbTeO$_3$ crystal phases were also found to be partly responsible for NLO effects. The observed maximal effect in $\Delta n$ at 570 nm is correlated with $^2B_{2g} \rightarrow ^2B_{1g}$ transition of Ti$^{3+}$ ions.

The objectives of the Chapter V is to determine piezoelectric coefficients coupled with elastic properties as a function of the concentration of crystallizing agent and to analyze the results within a framework of different crystal phases formed in the glass ceramics.

The variation of measured piezoelectric coefficient $d_{33}$ for ZnF$_2$–PbO–TeO$_2$: TiO$_2$ glass ceramic with the concentration of nucleating agent TiO$_2$ exhibited maximal effect at $x = 1.0$ wt%. From the XRD studies of these samples it is evidenced that the presence of higher concentration of Pb$_5$Ti$_3$F$_{19}$ ferroelectric crystal phases in the glass ceramic sample TC$_{10}$. The structure of Pb$_5$Ti$_3$F$_{19}$ crystal phase consists of infinite chains of eclipsed corner-sharing TiF$_6$ octahedra as well as individual octahedrons. These phases contribute more
to the piezoelectric coefficient $d_{33}$ and were found to be responsible for higher value of $d_{33}$ for the samples crystallized with 1.0 wt% of TiO$_2$. The analysis of these results further indicated that other asymmetric crystal phases like PbTiO$_3$ and PbTeO$_3$ also contribute to the piezoelectric coefficient $d_{33}$ especially in the samples containing more than 1.0 wt% of TiO$_2$.

The ultrasonic velocities and elastic coefficients measured as a function of TiO$_2$ concentration were found to be the lowest for the samples crystallized with 1.0 wt% of TiO$_2$. This is ascribed to the larger presence of titanium ions in Ti$^{3+}$ states in this sample that will inculcate more degree of disorder in the glass ceramic network and thereby hamper the propagation of sound waves in the glass ceramic.

In Chapter VI we have reported the results of dielectric dispersion, ac conductivity, $\sigma_{ac}$, impedance spectra and electric modulus, $M(\omega)$ of ZnF$_2$–PbO–TeO$_2$ glasses crystallized with different concentrations of TiO$_2$ over a frequency range of $10^{-2}$ to $10^6$ Hz and within the temperature range 303 to 523 K and also dc conductivity over a wide temperature range and attempt is made to understand the conduction phenomenon as a function of concentration of crystallizing agent TiO$_2$. The obtained results were compared with principal results concerning the piezoelectric and photoinduced studies.

The observed increase of dielectric constant, $\varepsilon'(\omega)$, with temperature especially at lower frequencies is explained based on the contribution of space
charge polarization. The ac conductivity exhibited maximal effect, whereas the activation energy for the conductivity demonstrated minimal magnitude at 1.0 wt% of the crystallizing agent TiO\textsubscript{2}. The low temperature part of ac conductivity could successfully be explained following QMT model. The analysis of the results of dc conductivity has indicated that when T > \(\theta_D/2\), the small polaron hopping model is appropriate. These results further indicated that there is a mixed conduction both ionic and electronic in these glasses. The dielectric relaxation effects exhibited by these samples have been analyzed quantitatively using graphical method. The variation of a.c. conductivity with the concentration of crystallizing agent is compared with those of second order susceptibility and the piezoelectric coefficient reported in earlier chapters. The comparison indicated the phenomena responsible for the maximal effects for all the three parameters at 1.0 wt% of TiO\textsubscript{2} are the same.

**Chapter-VII** reports brief summary and conclusions drawn from the investigation carried out on a variety of properties viz., dielectric, spectroscopic properties, non-linear optical properties, piezoelectric properties and elastic properties of ZnF\textsubscript{2}–PbO–TeO\textsubscript{2} glasses crystallized with different concentrations of TiO\textsubscript{2}. References closely related to the present work have been compiled to the extent possible and given at the end of the relevant chapter.