PREFACE

The present work concerns with the "**Spectroscopic and Dielectric Investigations on ZnF_2–As_2O_3–TeO_2: V_2O_5/NiO Glass System and Fluorescence Features of Some Rare Earth ions in ZnF_2–WO_3–TeO_2 Glass System**". 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 dielectric, spectroscopic properties of ZnF_2–As_2O_3–TeO_2 glass system doped with V_2O_5 and NiO and also optical absorption and fluorescence studies of ZnF_2–WO_3–TeO_2 system doped with three rare earth ions (viz., Nd^{3+}, Sm^{3+} and Eu^{3+}).

Among various glass systems tellurium oxide based glasses are the subject of intense current research because of their interesting 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 third order non-linear susceptibility, good chemical resistance and good infrared transmissivity.

In view of these qualities, tellurite based glasses were considered as potential candidates for laser hosts (since these provide a low phonon energy environment to minimize non-radiative loss), in fiber optics, as nonlinear optical materials, as the best materials for optical components such as IR domes, optical filters, modulators, memories and laser windows.

Tellurium oxide is an incipient glass network former; hence the addition of strong network former like As_2O_3 to tellurium oxide glasses improves the glass forming ability and the optical transparency in the blue as well as in the IR regions. As_2O_3 is the only strong network former besides GeO_2 that exhibit significant transmission potential farther into the infrared. The addition of As_2O_3 is expected to affect the infrared transmission of TeO_2 glasses to a less extent, since the frequencies of some of the fundamental modes of vibration of As_2O_3 structural groups lay in the region of vibrations of TeO_4 structural groups. In view of this, it is also predicted that AsO_3 groups form a single arsenic–tellurium–oxygen framework with the TeO_4 structural units and may strengthen the glass network. Addition of the modifier like ZnF_2 to TeO_2–As_2O_3 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.

Similarly, the addition of WO_3 to tellurite glasses makes them suitable for optoelectronic devices since they exhibit photochromism and electrochromism properties and influences profoundly the luminescence characteristics of rare earth ions in tellurite glasses, since these ions exist in different valence states viz., W^{6+}, W^{5+} and also in W^{4+} and offer varying environment for luminescent ions in the glass network.

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 electrical properties, especially on dielectric relaxation and ac conductivity of $ZnF_2–As_2O_3–TeO_2$ glass system doped with transition metal ions like V_2O_5 and NiO are very rare; knowledge on these properties is highly helpful for estimating the influence of these oxides on the insulating strength of tellurite glasses and may also pave way for the analysis of the structure of this glass system to some extent if these studies are coupled with the other studies like optical absorption, ESR, infrared, Raman and luminescence spectra.

As mentioned above the tellurite glasses mixed with WO_3 offers highly suitable environment for hosting the rare earth ions to give out high luminescence output with low phonon losses. In view of this, a part of the thesis is devoted to investigate the fluorescence characteristics of three interested rare earth ions viz., Nd^{3+}, Sm^{3+} and Eu^{3+} ions in $ZnF_2–WO_3–TeO_2$ glass system.

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

- To have a comprehensive understanding over the influence of **vanadium** ions on structural aspects of $ZnF_2–As_2O_3–TeO_2$ glasses by

investigating the dielectric properties, optical absorption, ESR, IR and photoluminescence.

- To have a broad perceptive over the role of **nickel** ions on the structure of ZnF_2–As_2O_3–TeO_2 glass system from a systematic study of various dielectric properties coupled with spectroscopic and magnetic studies.
- To investigate the luminescence efficiencies of three rare earth ions (viz., **Nd^{3+}, Sm^{3+} and Eu^{3+}**) in ZnF_2–WO_3–TeO_2 glasses and to examine the possible uses of these glasses laser hosts.

The glasses used for the present studies are:

1. V_2O_5 series: $20ZnF_2$–$30As_2O_3$–$(50–x)\ TeO_2$: $x\ V_2O_5$ $(0 \le x \le 0.6)$
2. NiO series: $20ZnF_2$–$30As_2O_3$–$(50–x)TeO_2$: $xNiO$ $(0 \le x \le 2.0)$
3. Ln_2O_3 series: $(50–x)ZnF_2$–xWO_3–$49TeO_2$: $1Ln_2O_3$ $(5 \le x \le 20)$

   (where Ln = Nd, Sm and Eu)

The studies carried out are

(i) differential scanning calorimetry and the evaluation of glass transition temperature T_g;

(ii) infrared spectral studies in the wavenumber range 400-2000 cm^{-1} and the study of the effect of concentration of transition metal ions on the position and intensity of various vibrational bands;

(iii) optical absorption studies in the wavelength range 300–2100 nm, identification of various electronic transitions of transition metal ions;

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

(v) dielectric properties viz., dielectric constant ε^{l}, dielectric loss tan δ and ac conductivity σ_{ac} in the frequency range 10^{2}–10^{5} Hz and in the temperature range 30–250 ^{o}C;

(vi) optical absorption, fluorescence studies of Nd^{3+}, Sm^{3+} and Eu^{3+} ions doped ZnF_2–WO_3–TeO_2 glasses.

For the sake of convenience the thesis is divided into five chapters.

Chapter–I presents the General Introduction, Scope, Contents and the Aim of the present work. In this chapter, the basic theory related to dielectric and spectroscopic properties of ZnF_2–As_2O_3/WO_3–TeO_2 glasses doped with transition metal ions and rare earth ions is presented systematically.

Chapter–II gives the description of experimental methods employed in the preparation and characterization ZnF_2–As_2O_3/WO_3–TeO_2 glasses. The details of the apparatus used and the techniques adopted for measuring dielectric properties, optical absorption, ESR, IR and luminescence are also described in detail in this chapter.

The scanning electron microscopy and X–ray diffraction studies have been carried out on all the three series of the samples doped with V_2O_5, NiO and Ln_2O_3; these studies have indicated virtually no crystallization.

Chapter-III The objective of this chapter is to have a comprehensive understanding over the topology and valence states of vanadium ions in $20ZnF_2–30As_2O_3–(50–x)\ TeO_2$: x V_2O_5 ($0 \leq x \leq 0.6$) glass network by a systematic study of dielectric properties over a wide range of frequency and temperature and spectroscopic properties (viz., optical absorption, photoluminescence, ESR and IR) studies.

The conclusions drawn from the study of various physical properties of these glasses are as follows:

The optical absorption spectra of these glasses have exhibited two clearly resolved bands due to $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2E$ transitions of vanadyl ions. The intensity and the half width of these bands have been observed to be maximal in the spectrum of glass V_6; from this observation it is concluded that VO^{2+} (vanadyl) ions present in larger concentrations in this glass network. The ESR spectra of $ZnF_2–As_2O_3–TeO_2$: V_2O_5 glasses recorded at room temperature are observed to be complex made up of resolved hyperfine components arising from unpaired $3d^1$ electron of ^{51}V isotope having spin 7/2. As the concentration of V_2O_5 is increased, an increase in the degree of resolution and the intensity of signal, have been observed. The quantitative analysis of the ESR spectra revealed that there is a progressive weakening of the bonding between V^{4+} ion and equatorial oxygen as the concentration of V_2O_5 is increased. From this analysis it is also concluded that there is an increase in the degree of disorder

of the octahedral and in the glass network as a whole with increase in the concentration of V_2O_5. The IR spectrum of pure glass exhibited a band due to ν_s-TeO_{2ax} (axial band) at about 643 cm^{-1} whereas the equatorial band viz., ν_s–TeO_{2eq} is observed to be missing; the spectra also exhibited bands due to ν_1 and ν_2–vibrations of AsO_3 structural groups. V_2O_5 doped glasses have exhibited two additional bands due to the vibrations of V–O–V chains. With the gradual increase in the concentration of V_2O_5, the ν_s–TeO_{2ax} and ν_2 of AsO_3 bands are shifted gradually towards considerably higher frequencies with decreasing intensity. Such changes have been understood due to increasing modifying action of vanadyl ions in the glass network with increase in the concentration of V_2O_5. The photoluminescence spectra of ZnF_2–As_2O_3–TeO_2: V_2O_5 glasses recorded at room temperature with the excitation wavelength of 640 nm exhibited a broad emission band in the region 750-850 nm due to $^2E \rightarrow {}^2T_2$ transition of vanadyl ion. With increase in the concentration of V_2O_5, the intensity of the peak is observed to increase with a red shift. The shift of this PL peak, the shape and the structured nature of the PL emission band have been identified as a signature of shallow levels with an electron–phonon coupling. The dielectric parameters viz., ε' tan δ and σ_{ac} are found to increase and the activation energy for ac conduction is found to decrease with the increase in the concentration of V_2O_5 up to 0.6 mol%. From this result it is concluded that there is a gradual increase in the concentration of V^{4+} ions those

act as modifiers in the glass network. The analysis of dielectric loss studies indicated that these glasses exhibit dipolar effects. The ac conduction could be explained both due to classical activation energy and due to the tunneling phenomena.

The objective of the **Chapter–IV** is to throw some light on the emission characteristics of nickel ions in the IR region in ZnF_2–As_2O_3–TeO_2 glass system. The studies undertaken are optical absorption, IR and photoluminescence after the characterization of the glasses by X–ray diffraction, energy dispersive spectroscopy and thermal analysis. The magnetic and dielectric studies are also taken up to have some additional information on the environment of the nickel ions in the glass matrix.

A particular composition $20ZnF_2$–$30As_2O_3$–$(50\text{-}x)TeO_2$: xNiO (with x ranging from 0 to 2.0) is chosen for this study.

The main conclusions drawn from this study are as follows:

The optical absorption spectra of NiO doped ZnF_2–As_2O_3–TeO_2 glasses exhibited, three clearly resolved intense absorption bands in the NIR and visible regions at 1310 nm (O_{h1}), 795 nm (O_{h2}) and 718 nm (T_{d2}); using T-S diagram for d^8– ions, these bands are attributed to the transitions $^3A_2(F)\rightarrow{}^3T_2(F)$, $^3A_2(F)\rightarrow{}^3T_1(F)$ and $^3T_1(F)\rightarrow{}^3T_1(P)$ respectively. As the concentration of NiO is increased, the intensity of the octahedral bands (O_h bands) is observed to increase with a shift towards slightly higher wavelength;

the intensity of the tetrahedral band is observed to decrease with a slight shift in the band position towards lower wavelength. The value of the optical band gap evaluated from the Urbach plots is found to be the highest for the glass N_2 and decreased with increase in the content of NiO.

The analysis of IR spectral studies of these glasses has indicated an increasing degree of disorder with increase in the concentration of NiO in the glass matrix. The magnetic susceptibility of these samples has also been measured and magnetic moments have been evaluated. The examination of these results has indicated that there is a gradual adaptation of nickel ions from tetrahedral to octahedral positions with increase in the concentration of NiO.

The photoluminescence spectra of NiO doped $ZnF_2–As_2O_3–TeO_2$ glasses, excited at 800 nm, have exhibited a broad band extending from 1200 to 1500 nm with the bary centre shifting towards slightly higher wavelengths with increase in the content of NiO. This emission band is attributed to $^3T_2(3F)\rightarrow{}^3A_2(3F)$ octahedral transition of Ni^{2+} ions. The width and the shape of this transition indicate that there is a relatively increased Stokes shift between the emission and absorption band.

The values of dielectric parameters viz., ε', tan δ and σ_{ac} at any frequency are found to increase with temperature and activation energy for ac conduction is observed to decrease with increase in the content of NiO; from this observation it is concluded that there is an increase in the space charge

polarization due to the increasing presence of octahedrally positioned nickel ions in the glass network. The variation of dielectric loss with temperature of these glasses has exhibited dielectric relaxation character. The analysis of these results has indicated the spreading of relaxation times. The dipolar effects have been attributed to the octahedral Ni^{2+} ions in addition to the Te–O linkages.

Chapter–V is devoted to investigate the fluorescence features of three different rare earth ions viz., Nd^{3+}, Sm^{3+} and Eu^{3+} ions in the visible and infrared regions in ZnF_2–WO_3–TeO_2 glass system with the gradual increase of WO_3 content in the glass network at the expense of ZnF_2. The results of ESR, IR and Raman spectral studies have also been used to have a comprehensive pre-knowledge over the structural changes in the glass network due to the variations in the concentrations of WO_3 at the vicinity of rare earth ions which influence the luminescence efficiency.

The optical absorption and fluorescence studies in the visible and NIR regions have also been carried out on ZnF_2–WO_3–TeO_2 glasses containing three rare earth ions viz., Nd^{3+}, Sm^{3+} and Eu^{3+} (with varying concentrations of WO_3) with a view to examine the possible use of these materials as laser hosts and to investigate the variations in the concentration of WO_3 on luminescence efficiencies.

The recorded **optical absorption** spectral profiles of rare earth ions doped ZnF_2–WO_3–TeO_2 glasses have revealed the following transitions:

Nd^{3+}: $^4I_{9/2} \rightarrow {}^2P_{1/2}$, $^2K_{15/2}+{}^2G_{9/2}+{}^2D_{3/2}+{}^4G_{11/2}$, $^4G_{9/2}$, $^2K_{13/2}+{}^4G_{7/2}$, $^4G_{5/2}+{}^2G_{7/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4F_{7/2}+{}^4S_{3/2}$, $^4F_{5/2}$ and $^4F_{3/2}$

Sm^{3+}: $^6H_{5/2} \rightarrow {}^4I_{13/2}$, $^4I_{11/2}$, $^6F_{11/2}$. $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$, $^6H_{15/2}$ and $^6F_{1/2}$,

Eu^{3+}: $^7F_0 \rightarrow {}^5D_2$, $^7F_6$, $^7F_5$ and $^7F_1 \rightarrow {}^5D_1$

With the increase in the concentration of WO_3, considerable variations in the spectral peak positions and the intensity of the bands have been observed. The experimental oscillator strengths (OS) of the absorption transitions were estimated from the spectra for all the three rare earth ion doped glasses in terms of the area under absorption peaks. The quality of fitting is determined by the root mean squared deviation between experimental and evaluated oscillatory strengths. The deviation indicates reasonably good fitting between theory and experiment demonstrating the applicability of JO theory.

The luminescence spectra of all the three series of glasses recorded at room temperature in the visible and NIR regions. The spectra exhibited the following prominent emission bands:

Nd^{3+}(λ_{exc}= 878 nm) : $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{11/2}$, $\mathbf{^4I_{13/2}}$

Sm^{3+} (λ_{exc}= 462 nm) : $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $\mathbf{^6H_{7/2}}$, $^6H_{9/2}$

Eu^{3+} (λ_{exc}= 465 nm) : $^5D_0 \rightarrow {}^7F_0$, $^7F_1$, $\mathbf{^7F_2}$, $^7F_3$, $^7F_4$

It is noticed that with increase in the content of WO_3 up to 15 mol%, the intensity of the three principal bands viz., $^4F_{3/2} \rightarrow {}^4I_{13/2}$ (Nd^{3+}), $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (Sm^{3+}), $^5D_0 \rightarrow {}^7F_2$ (Eu^{3+}) is observed to increase.

The summary of various radiative parameters connected with prominent luminescent transitions for these glasses containing 10 mol% of WO_3 are furnished in the following Table 1.

Table 1 Summary of the data on various radiative properties of different rare-earth ions doped ZnF_2–TeO_2 glasses mixed with 15 mol% of WO_3.

RE & Emission Transition	Energy (cm^{-1})	A (s^{-1})	A_T (s^{-1})	β%
Nd^{3+}: $^4F_{3/2} \rightarrow {}^4I_{11/2}$	9512	4788.0	9346	51.23
Sm^{3+}: $^4G_{5/2} \rightarrow {}^6H_{7/2}$	16669	243.1	448	54.26
Eu^{3+}: $^5D_0 \rightarrow {}^7F_2$	16234	253.7	340	74.62

The comparison of radiative life times and quantum yields for glasses for the principal transitions of the three rare earth ions in ZnF_2–WO_3–TeO_2 glasses is presented in Table 2.

Table 2 The comparison table of radiative life times and quantum yields

WO_3 conc. (mol %)	Nd^{3+} doped glasses ($^4F_{3/2}$ level)			Sm^{3+} doped glasses ($^4G_{5/2}$ level)			Eu^{3+} doped glasses ($^5D_0$ level)		
	(τ_m) μs	(τ_c) μs	(η%)	(τ_m) ms	(τ) ms	(η%)	(τ_m) ms	(τ) ms	(η%)
5	65.14	95	68.57	0.98	1.60	61.25	1.04	2.50	41.60
10	82.52	107	77.12	1.48	2.20	67.27	1.27	2.90	43.79
15	102.06	116	87.98	1.93	2.72	70.96	1.69	3.25	52.0
20	91.20	109	83.67	1.80	2.61	68.97	1.39	2.85	48.77

The quantitative analysis of these results, with the aid of the data on ESR, IR and Raman spectral studies, it is concluded that the glass containing around 15 mol% of WO_3 have exhibited the highest luminescence efficiency for all the three rare earth ions.

Chapter-VI reports brief summary and conclusions drawn from the investigation carried out on a variety of properties viz., dielectric and spectroscopic properties of ZnF_2–As_2O_3/WO_3–TeO_2 glass system doped with transition ions (vanadium and nickel) and spectroscopic properties doped with rare earth ions.

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