Chapter 6

Summary and Conclusions

This chapter contains a brief outline and conclusions drawn from the investigation carried out on (a) electrical properties and (b) spectroscopic properties of V_2O_5 and NiO doped ZnF_2-As_2O_3-TeO_2 glasses. Outlines of optical absorption and luminescence spectroscopy of rare earth ions (viz., Nd^{3+}, Sm^{3+} and Eu^{3+}) in ZnF_2-WO_3-TeO_2 glass systems are also presented.

Summary and Conclusions

6.1 Summary

ZnF_2–As_2O_3–TeO_2 glasses with two dopants viz., V_2O_5 and NiO and also ZnF_2–WO_3–TeO_2 glasses doped with three rare earth ions (viz., Nd^{3+}, Sm^{3+} and Eu^{3+}) have been synthesized. A systematic investigation on characterization (viz., XRD, SEM, EDS & DSC studies) and physical properties (viz., dielectric properties, infrared, Raman, optical absorption, ESR and photoluminescence spectra) have been studied.

The compositions of the samples used for the present study are

10. V_2O_5 series: $20ZnF_2$–$30As_2O_3$–$(50–x)\ TeO_2$: $x\ V_2O_5$ $(0 \le x \le 0.6)$
11. NiO series: $20ZnF_2$–$30As_2O_3$–$(50–x)TeO_2$: xNiO $(0 \le x \le 2.0)$
12. 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 glasses were prepared by the usual melting, quenching and subsequent annealing techniques. The samples were characterized by X–ray diffraction, scanning electron microscopy, EDS and DSC techniques.

The following measurements were taken:

1) Dielectric constant (ε^{l}), loss (tan δ) and ac conductivity σ_{ac} in frequency range 10^2 to 10^5 Hz and in the temperature range 30-250^{o}C.

2) Optical absorption and photoluminescence in the UV, visible and NIR regions

3) Electron spin resonance spectra of V_2O_5 doped glasses at room temperature.

4) Infrared and Raman spectra of all these glasses in the region 400 to 4000 cm^{-1}.

6.2 Conclusions

The main conclusions drawn form the results of above studies are summarized below:

- The **scanning electron microscopic** (SEM) pictures and **X-ray diffraction** of the samples prepared containing different concentration of transition metal oxides do not show any crystallinity. **The EDS analysis** of the glasses indicate the presence of Te, Zn, As, W, O and V/Ni/Nd/Sm/Eu elements in the samples.
- The **differential scanning calorimetric** studies (DSC) of all the samples exhibited endothermic change due to the glass transition followed by exothermic effect due to the crystal growth and an endothermic peak due to re-melting of the samples. The glass forming ability parameter is found to be decreasing gradually with increase in the concentration of V_2O_5 and NiO in the ZnF_2–As_2O_3–TeO_2 glass

matrix. Where as for the rare earth doped tungsten tellurite glasses the parameter is found to decrease with increase of WO_3 up to 15 mol% and for further increase this parameter is found to increase.

- The summary of the results on studies of dielectric properties of **ZnF_2–As_2O_3–TeO_2: V_2O_5** glasses coupled with spectroscopic studies is 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 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 luminescence 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 a.c. 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.

- **Conclusions from the studies on rare earth ions mixed ZnF_2–WO_3–TeO_2 glasses**

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:

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

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

Eu^{3+} ($\lambda_{exc}= 465$ 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 6.1.

Table 6.1 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 6.2.

Table 6.2 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.

Summing up the entire work presented in this thesis it is felt that the study of various electrical and spectroscopic properties of ZnF_2–As_2O_3–TeO_2 glasses doped with different concentrations of V_2O_5 and NiO and spectroscopic studies of ZnF_2–WO_3–TeO_2: Ln^{3+} (Nd^{3+}, Sm^{3+} and Eu^{3+}) glasses have yielded some valuable information which will be useful for the practical applications of these materials.