Spectral and Thermal Properties of Er^{3+} Doped Zinc Lithium Alumino Tungsten Borophosphate Glasses

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***Abstract*: Zinc lithium alumino tungsten borophosphate glasses containing Er^{3+} in $(35-x):P_2O_5:10ZnO:10Li_2O:10Al_2O_3:10WO_3:25B_2O_3:xEr_2O_3$. (Where x=1, 1.5,2 mol %) have been prepared by melt-quenching method. The amorphous nature of the glasses was confirmed by x-ray diffraction studies. Optical absorption and fluorescence spectra were recorded at room temperature for all glass samples. Judd-Ofelt intensity parameters Ω_λ (λ=2, 4, 6) are evaluated from the intensities of various absorption bands of optical absorption spectra. Using these intensity parameters various radiative properties like spontaneous emission probability, branching ratio, radiative life time and stimulated emission cross–section of various emission lines have been evaluated.**

***Keywords*: ZLATBP Glasses, Optical Properties, Judd-Ofelt Theory, Thermal Properties.**

1. Introduction

Rare earth glasses have attracted much attention, because they have large practical and potential applications in many fields, such as glass lasers, optical fiber amplifiers, phosphors, electro-luminescent devices, photo chemical and mechanical stability [1-8]. Glass–ceramics could be classified in transparent or opaque glass–ceramic depending on their transmittance, which depends in a sensitive way on the annealing condition used to induce crystallization [9]. The phosphate glasses show the broadband transmission window, the high linear and nonlinear refractive indices, the low phonon energy and the high rare-earth solubility. Phosphate glasses are very well known for their suitable mechanical and chemical properties, homogeneity, good thermal stability, and excellent optical properties [10–15]. They present superior properties that include high transparency, low melting point, high thermal stability, high gain density, high solubility for rare-earth ions and low dispersion [16].Zinc oxide operates as a stabilizer substance in the glass network of ternary and quaternary glass. With the addition of zinc oxide, it will raise the surface tension of the molten and recover the crystallization stability within the substance of the existing section. Among the different oxide components, such as SiO_2, WO_3 or P_2O_5, successfully used for glass synthesis, B_2O_3 is the best glass-former, which makes glass with high chemical durability and thermal stability, good transparency and rare earths solubility.

The aim of the present study is to prepare the Er^{3+} doped zinc lithium alumino tungsten borophosphate glass with different Er_2O_3 concentrations. The absorption spectra, fluorescence spectra of $Er^{3+}$of the glasses were investigated. The Judd-Ofelt theory has been applied to compute the intensity parameters Ω_λ (λ=2, 4, 6).These intensity parameter have been used to evaluate optical properties such as spontaneous emission probability, branching ratio, radiative life time and stimulated emission cross section.

2. Experimental Techniques

Preparation of glasses

The following Er^{3+} doped zinc lithium alumino tungsten borophosphate glass samples $(35-x):P_2O_5:10ZnO:10Li_2O:10Al_2O_3:10WO_3:25B_2O_3:xEr_2O_3$. (where x=1, 1.5.2) have been prepared by melt-quenching method. Analytical reagent grade chemical used in the present study consist of P_2O_5, ZnO, Li_2O, Al_2O_3, WO_3, B_2O_3 and Er_2O_3. All weighed chemicals were powdered by using an Agate pestle mortar and mixed thoroughly before each batch (10g) was melted in alumina crucibles in silicon carbide based an electrical furnace.

Silicon Carbide Muffle furnace was heated to working temperature of 1055^0C, for preparation of zinc lithium alumino tungsten borophosphate glasses, for two hours to ensure the melt to be free from gases. The melt was stirred several times to ensure homogeneity. For quenching, the melt was quickly poured on the steel plate & was immediately inserted in the muffle furnace for annealing. The steel plate was preheated to100^0C.While pouring; the temperature of crucible was also maintained to prevent crystallization. And annealed at temperature of 350^0C for 2h to remove thermal strains and stresses. Every time fine powder of cerium oxide was used for polishing the samples. The glass samples so prepared were of good optical quality and were transparent. The chemical compositions of the glasses with the name of samples are summarized in Table 1.

Table 1 Chemical composition of the glasses

Sample	Glass composition (mol %)
ZLATBP (UD)	35 P_2O_5:10ZnO:10Li_2O: 10Al_2O_3: 10WO_3:25 B_2O_3
ZLATBP (ER 1)	34 P_2O_5:10ZnO:10Li_2O: 10Al_2O_3: 10WO_3:25 B_2O_3: 1 Er_2O_3
ZLATBP (ER 1.5)	33.5 P_2O_5:10ZnO:10Li_2O: 10Al_2O_3: 10WO_3:25 B_2O_3:1.5 Er_2O_3
ZLATBP (ER 2)	33 P_2O_5:10ZnO:10Li_2O: 10Al_2O_3: 10WO_3:25 B_2O_3:2 Er_2O_3

ZLATBP (UD)—Represents undoped Zinc Lithium Alumino Tungsten Borophosphate glass specimens.

ZLATBP (ER) -Represents Er^{3+} doped Zinc Lithium Alumino Tungsten Borophosphate glass specimens.

3. THEORY

3.1 Oscillator Strength

The intensity of spectral lines are expressed in terms of oscillator strengths using the relation [17].

$$f_{expt.} = 4.318 \times 10^{-9} \int \varepsilon(\nu)\, d\nu \qquad (1)$$

where, ε (*ν)* is molar absorption coefficient at a given energy *ν* (cm^{-1}), to be evaluated from Beer–Lambert law.

Under Gaussian Approximation, using Beer–Lambert law, the observed oscillator strengths of the absorption bands have been experimentally calculated, using the modified relation [18].

$$P_m = 4.6 \times 10^{-9} \times \frac{1}{cl} \log \frac{I_0}{I} \times \Delta\upsilon_{1/2} \qquad (2)$$

where c is the molar concentration of the absorbing ion per unit volume, I is the optical path length, $\log I_0/I$ is absorptivity or optical density and $\Delta\upsilon_{1/2}$ is half band width.

3.2. Judd-Ofelt Intensity Parameters

According to Judd [19] and Ofelt [20] theory, independently derived expression for the oscillator strength of the induced forced electric dipole transitions between an initial J manifold $|4f^N (S, L) J\rangle$ level and the terminal J' manifold $|4f^N (S', L') J'\rangle$ is given by:

$$\frac{8\Pi^2 mc\bar{\upsilon}}{3h(2J+1)} \frac{1}{n}\left[\frac{(n^2+2)^2}{9}\right] \times S(J, J') \qquad (3)$$

where, the line strength S (J, J') is given by the equation

$$S(J, J') = e^2 \sum \Omega_\lambda \langle 4f^N (S, L)\, J \| U^{(\lambda)} \| 4f^N (S', L')\, J' \rangle^2 \qquad (4)$$

$\lambda = 2, 4, 6$

In the above equation m is the mass of an electron, c is the velocity of light, *ν* is the wave number of the transition, h is Planck's constant, n is the refractive index, J and J' are the total angular momentum of the initial and final level respectively, Ω_λ ($\lambda = 2, 4$ and 6) are known as Judd-Ofelt intensity parameters.

3.3. Radiative Properties

The Ω_λ parameters obtained using the absorption spectral results have been used to predict radiative properties such as spontaneous emission probability (A) and radiative life time (τ_R) and laser parameters like fluorescence branching ratio (β_R) and stimulated emission cross section (σ_p).

The spontaneous emission probability from initial manifold $|4f^N (S', L') J'\rangle$ to a final manifold $|4f^N (S, L)\, J\rangle|$ is given by:

$$A[(S', L')\,J'; (S, L)\,J] = \frac{64\,\pi^2 \nu^3}{3h(2J'+1)}\left[\frac{n(n^2+2)^2}{9}\right] \times S(J', \bar{J}) \qquad (5)$$

Where, $S(J', J) = e^2 [\Omega_2 \| U^{(2)} \|^2 + \Omega_4 \| U^{(4)} \|^2 + \Omega_6 \| U^{(6)} \|^2]$

The fluorescence branching ratio for the transitions originating from a specific initial manifold $|4f^N (S', L')\,J'>$ to a final many fold $|4f^N (S, L)\,J>$ is given by

$$\beta[(S', L')\,J'; (S, L)\,J] = \sum_{S\,L\,J} \frac{A[(S'\,L)]}{A[(S'\,L')\,J'(\bar{S}\,L)]} \qquad (6)$$

where, the sum is over all terminal manifolds.

The radiative life time is given by

$$\tau_{rad} = \sum_{S\,L\,J} A[(S', L')\,J'; (S, L)] = A_{Total}^{-1} \qquad (7)$$

where, the sum is over all possible terminal manifolds. The stimulated emission cross -section for a transition from an initial manifold $|4f^N (S', L')\,J'>$ to a final manifold $|4f^N (S, L)\,J>|$ is expressed as

$$\sigma_p(\lambda_p) = \left[\frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{eff}}\right] \times A[(S', L')\,J'; (\bar{S}, \bar{L})\bar{J}] \qquad (8)$$

where, λ_p the peak fluorescence wavelength of the emission band and $\Delta\lambda_{eff}$ is the effective fluorescence line width.

4. Result and Discussion

4.1. XRD Measurement

Figure 1 presents the XRD pattern of the samples containing show no sharp Bragg's peak, but only a broad diffuse hump around low angle region. This is the clear indication of amorphous nature with in the resolution limit of XRD instrument.

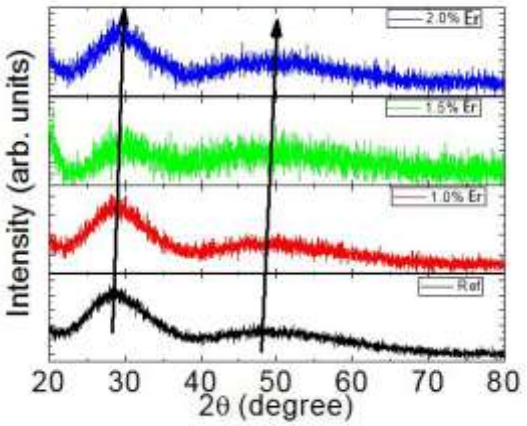

Fig.1: X-ray diffraction pattern of ZLATBP (ER) glasses.

4.2 Thermal Properties

Figure 2 shows the thermal properties of ZLATBP glass from 300^0C to 1000^0C. From the DSC curve of present glasses system, I can find out that no crystallization peak is apparent and the glass transition temperature T_g are 350^0C, 455^0C and 585^0C respectively. The T_g increase with the contents of Er_2O_3 increase. I could conclude that thermal properties of the ZLATBP glass are good for fiber drawing from the analysis of DSC curve.

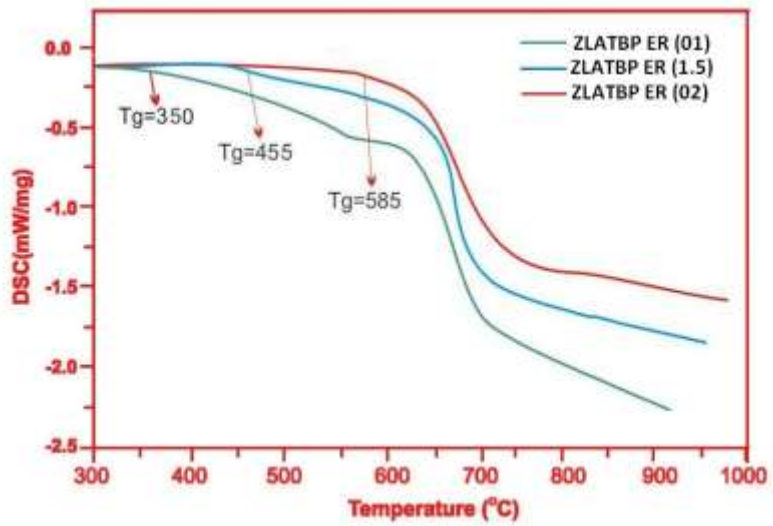

Fig.2: DSC curve of ZLATBP (ER) glasses.

4.3. Absorption spectra

The absorption spectra of ZLATBP (ER) glasses, consists of absorption bands corresponding to the absorptions from the ground state $^4I_{15/2}$ of Er^{3+} ions. Ten absorption bands have been observed from the ground state $^4I_{15/2}$ to excited states $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$, $^2H_{9/2}$ and $^4G_{11/2}$ for Er^{3+} doped ZLATBP (ER) glasses.

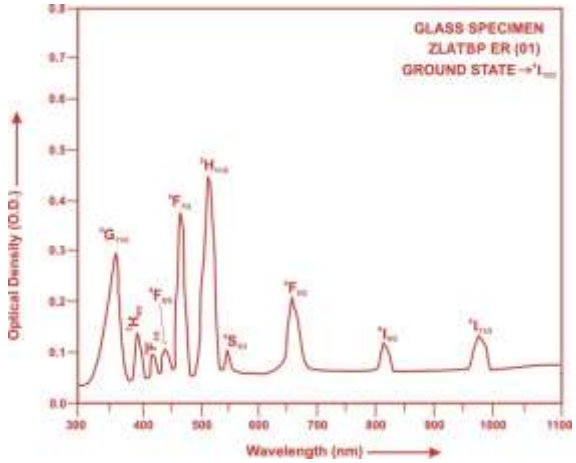

Fig.3: Absorption spectra of ZLATBP (ER) glasses.

The experimental and calculated oscillator strengths for Er^{3+} ions in zinc lithium alumino tungsten borophosphate glasses are given in **Table 2.**

Table 2. Measured and calculated oscillator strength ($P^m \times 10^{+6}$) of Er^{3+} ions in ZLATBP glasses.

Energy level $^4I_{15/2}$	Glass ZLATBP (ER01)		Glass ZLATBP (ER1.5)		Glass ZLATBP (ER02)	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^4I_{11/2}$	0.88	0.78	0.82	0.77	0.76	0.78
$^4I_{9/2}$	0.45	0.15	0.41	0.15	0.35	0.14
$^4F_{9/2}$	2.45	1.63	2.38	1.62	2.32	1.60
$^4S_{3/2}$	0.38	0.71	0.32	0.70	0.28	0.71
$^2H_{11/2}$	6.46	2.60	6.41	2.59	6.35	2.60
$^4F_{7/2}$	5.55	2.44	5.51	2.42	5.46	2.43
$^4F_{5/2}$	0.58	0.90	0.52	0.89	0.47	0.90
$^4F_{3/2}$	0.34	0.55	0.28	0.55	0.22	0.55
$^2H_{9/2}$	1.66	1.05	1.61	1.04	1.56	1.05
$^4G_{11/2}$	4.67	6.35	4.59	6.34	4.52	6.34
R.m.s.deviation	1.6980		1.6871		1.6693	

The various energy interaction parameters like Slater-Condon parameters F_k (k=2, 4, 6), Lande' parameter (ξ_{4f}) and Racah parameters E^k (k=1, 2, 3) have been computed using partial regression method and formula described elsewhere [21]. The ratio of Racah parameters E^1/E^3 and E^2/E^3 are about 10.348 and 0.0487 respectively. Which are almost equal to the hydrogenic ratio [22].

Table3. Computed values of Slater-Condon, Lande', Racah, nephelauexetic ratio and bonding parameter for Er^{3+} doped ZLATBP glass specimens.

Parameter	Free ion	ZLATBP ER01	ZLATBP ER1.5	ZLATBP ER02
$F_2(cm^{-1})$	441.680	433.885	433.877	433.841
$F_4(cm^{-1})$	68.327	67.049	67.047	67.056
$F_6(cm^{-1})$	7.490	7.0405	7.0380	7.0378
$\xi_{4f}(cm^{-1})$	2369.400	2414.791	2414.869	2414.849
$E^1(cm^{-1})$	6855.300	6661.703	6661.041	6660.942
$E^2(cm^{-1})$	32.126	31.336	31.333	31.3264
$E^3(cm^{-1})$	645.570	643.678	643.737	643.700
F_4/F_2	0.15470	0.15453	0.15453	0.15456
F_6/F_2	0.01696	0.016227	0.0162212	0.016222
E^1/E^3	10.61899	10.34943	10.34746	10.34790
E^2/E^3	0.049764	0.0486827	0.0486736	0.048666
β'		0.98235	0.98233	0.98225
$b^{1/2}$		0.093941	0.093995	0.94207

Judd-Ofelt intensity parameters Ω_λ (λ = 2, 4 and 6) were calculated by using the fitting approximation of the experimental oscillator strengths to the calculated oscillator strengths with respect to their electric dipole contributions. In the present case the three Ω_λ parameters follow the trend $\Omega_4 < \Omega_2 < \Omega_6$.

The values of Judd-Ofelt intensity parameters are given in **Table 4**.

Table 4. Judd-Ofelt intensity parameters for Er^{3+} doped ZLATBP glass specimens.

Glass Specimen	$\Omega_2(pm^2)$	$\Omega_4(pm^2)$	$\Omega_6(pm^2)$	Ω_4/Ω_6
ZLATBP (ER01)	0.8289	0.2851	0.9924	0.287
ZLATBP (ER1.5)	0.8339	0.2765	0.9869	0.280
ZLATBP (ER02)	0.8407	0.2648	0.9905	0.267

4.4. Fluorescence Spectrum

The fluorescence spectrum of Er^{3+}doped in zinc lithium alumino tungsten borophosphate glass is shown in Figure4. There are four broad bands ($^4F_{7/2}\rightarrow{}^4I_{15/2}$), ($^2H_{11/2}\rightarrow{}^4I_{15/2}$) ($^4S_{3/2}\rightarrow{}^4I_{15/2}$) and ($^4F_{9/2}\rightarrow{}^4I_{15/2}$) respectively for glass specimens.

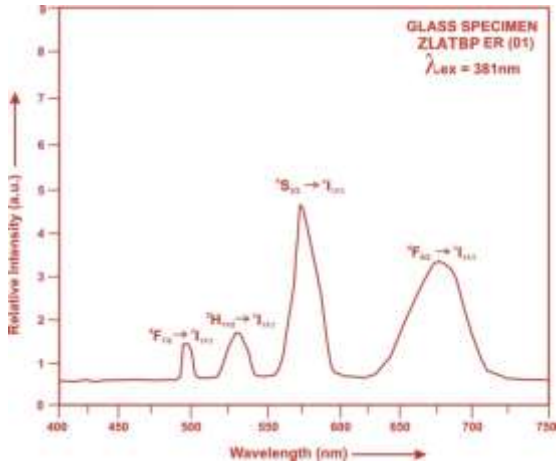

Fig.4: Fluorescence spectrum of ZLATBP glasses doped with Er^{3+}.

Table 5. Emission peak wave lengths (λ_p), radiative transition probability (A_{rad}), branching ratio (β_R), stimulated emission crosssection (σ_p), and radiative life time (τ) for various transitions in Er^{3+} doped ZLATBP glasses.

	ZLATBP (ER01)					ZLATBP (ER1.5)				ZLATBP (ER02)			
Transition	λ_p(nm)	$A_{rad}(s^{-1})$	β_R	σ_p ($10^{-20}cm^2$)	τ_R(μs)	$A_{rad}(s^{-1})$	β_R	σ_p ($10^{-20}cm^2$)	τ_R(μs)	$A_{rad}(s^{-1})$	β_R	σ_p ($10^{-20}cm^2$)	τ_R(μs)
$^4F_{7/2}\rightarrow{}^4I_{15/2}$	490	2668.13	0.4325	0.6246	161.63	2651.04	0.4306	0.6033	162.43	2659.88	0.4309	0.5875	162.02
$^2H_{11/2}\rightarrow{}^4I_{15/2}$	535	1552.56	0.2509	0.4195		1552.82	0.2522	0.4101		1557.37	0.2523	0.4012	
$^4S_{3/2}\rightarrow{}^4I_{15/2}$	554	1188.08	0.1920	0.3066	246.28	1182.50	0.1921	0.3013	266.79	1188.48	0.1926	0.2951	271.92
$^4F_{9/2}\rightarrow{}^4I_{15/2}$	662	778.1.67	0.1258	0.3576		770.25	0.1251	0.3478		766.28	0.1242	0.3397	

5. Conclusion

In the present study, the glass samples of composition (35-x) P_2O_5:10ZnO:10Li_2O: 10Al_2O_3:10WO:25B_2O_3:xEr_2O_3 (where x =1, 1.5, 2 mol %) have been prepared by melt-quenching method. The value of stimulated emission cross-section (σ_p) is found to be maximum for the transition ($^4F_{7/2}\rightarrow{}^4I_{15/2}$) for glass ZLATBP (ER 01), suggesting that glass ZLATBP (ER 01) is better compared to the other two glass systems ZLATBP (ER1.5) and ZLATBP (ER02).

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