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SPECTRAL AND THERMAL PROPERTIES OF TB^{3+} DOPED IN ZINC LEAD LITHIUM BOROTENGSTEN TELLURITE GLASSES

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ABSTRACT

Glass sample of Zinc Lead Lithium Borotengsten Tellurite (35-x) TeO_2: 10ZnO: $10Li_2O$:10PbO: $15Wo_3$:20 B_2O_3: x Tb_2O_3. (where x=1,1.5,2 mol%) have been prepared by melt-quenching technique. The amorphous nature of the prepared glass samples was confirmed by X-ray diffraction. The absorption spectra of three Tb^{3+} doped zinc lead lithium borotengsten tellurite glasses have been recorded at room temperature. The various interaction parameters like Slater-Condon parameters F_2, Lande' parameter (ξ_{4f}), nephelauexetic ratio (β'), bonding parameter ($b^{1/2}$) and Racah parameters E^k (k=1, 2, 3) have been computed. Judd-Ofelt intensity parameters Ω_λ (λ = 2, 4, 6) and laser parameters have also been calculated. The spectroscopic quality factor related with the rigidity of the glass system is also discussed.

Keywords: *Tengsten tellurite glasses, Energy interaction parameters, Optical properties, Judd-Ofelt analysis*

1. INTRODUCTION

Rare-earth ions doped glasses are very attractive and have drawn a great deal of interest in the fields of photonics and optoelectronic materials development [1-4].Tellurite glasses are very promising materials for laser and non-linear applications in optics, due to some of their important characteristic features, such as high refractive index and low phonon maxima [5-7]. Tellurite glass has a low melting point and is nonhygroscopic, which is an advantage when compared to borate and phosphate glasses. These types of glasses are extremely stable against devitrification, nontoxic and resistant to moisture for long periods of time [8]. In recent years, optical properties of rare earth (RE) doped luminescent materials have been widely investigated and found to have important applications such as lasers, fiber amplifiers, full-color display devices and white light emitting diodes [9-14].Comparing with halide and sulfide glasses, oxide glasses are considered to be with more stable chemical durability and higher phonon energies [15,16].

The aim of the present study is to prepare the Tb^{3+} doped zinc lead lithium borotengsten tellurite glass with different Tb_2O_3 concentrations. The absorption spectra, fluorescence spectra of $Tb^{3+}$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 Tb^{3+} doped Tellurite glass samples (35-x) TeO_2: 10ZnO: $10Li_2O$:10PbO: $15Wo_3$:20 B_2O_3: x Tb_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 TeO_2, Wo_3, Li_2O, B_2O_3, ZnO, PbO and Tb_2O_3. They were thoroughly mixed by using an agate pestle mortar. then melted at 900^0C by an electrical muffle furnace for 2h., After complete melting, the melts were quickly poured in to a preheated stainless steel mould and annealed at temperature of 200^0C 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 %)
ZLLBTT (UD)	35TeO_2: 10ZnO: 10Li_2O:10PbO: 15Wo_3:20 B_2O_3
ZLLBTT (TB1)	34TeO_2: 10ZnO: 10Li_2O:10PbO: 15Wo_3:20 B_2O_3:1 Tb_2O_3.
ZLLBTT (TB1.5)	33.5TeO_2: 10ZnO: 10Li_2O:10PbO: 15Wo_3:20 B_2O_3: 1.5 Tb_2O_3.

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ZLLBTT (TB 2) $33TeO_2$: 10ZnO: $10Li_2O$:10PbO: $15Wo_3$:20 B_2O_3: 2 Tb_2O_3.
ZLLBTT (UD) -Represents undoped Zinc Lead Lithium Borotengsten Telluritespecimen.
ZLLBTT (TB) -Represents Tb^{3+} doped Zinc Lead Lithium Borotengsten Tellurite glass specimens.

3. THEORY

3.1 Oscillator Strength
The spectral intensity is 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 (*v)* is molar absorption coefficient at a given energy *v* (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 [18], using the modified relation:

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

Where c is the molar concentration of the absorbing ion per unit volume, *l* is the optical path length, $\log I_0/I$ is 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> level and the terminal J' manifold $|4f^N$ (S',L') J'> 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

$$S(J, J') = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda <4f^N(S, L) J \| U^{(\lambda)} \| 4f^N (S', L') J'>^2$$

In the above equation m is the mass of an electron, c is the velocity of light, *v* 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 (λ = 2, 4, 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'> to a final manifold $|4f^N$ (S, L) J >| is given by:

$$A[(S', L') J'; (S, L) J] = \frac{64\pi^2\nu^3}{3h(2J'+1)}\left[\frac{n(n^2+2)^2}{9}\right]\times S(J',\bar{J}) \qquad (4)$$

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

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

$$\beta[(S', L') J'; (S, L) J] = \sum_{SLJ} \frac{A[(S' \; L)]}{A[(S' \; L') \; J'(\bar{S} \; L)]} \quad (5)$$

Where, the sum is over all terminal manifolds.

The radiative life time is given by

$$\tau_{rad} = \sum_{SLJ} A[(S', L') J'; (S,L)] = A_{Total}^{-1} \quad (6)$$

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

$$\sigma_p(\lambda_p) = \left[\frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{eff}}\right] \times A[(S',L') J'; (\bar{S},\bar{L})\bar{J}] \quad (7)$$

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

3.4 Nephelauxetic Ratio (β) and Bonding Parameter ($b^{1/2}$)

The nature of the R-O bond is known by the Nephelauxetic Ratio (β') and Bonding Parameter ($b^{1/2}$), which are computed by using following formulae [21, 22]. The Nephelauxetic Ratio is given by

$$\beta' = \frac{\nu_g}{\nu_a} \quad (8)$$

Where, ν_g and $\nu_a$refer to the energies of the corresponding transition in the glass and free ion, respectively. The values of bonding parameter ($b^{1/2}$) is given by

$$b^{1/2} = \left[\frac{1-\beta'}{2}\right]^{1/2} \quad (9)$$

4. RESULT AND DISCUSSION

4.1 XRD Measurement

Figure 1 presents the XRD pattern of the sample contain - B_2O_3 which is show no sharp Bragg's peak, but only a broad diffuse hump around low angle region. This is the clear indication of amorphous nature within the resolution limit of XRD instrument.

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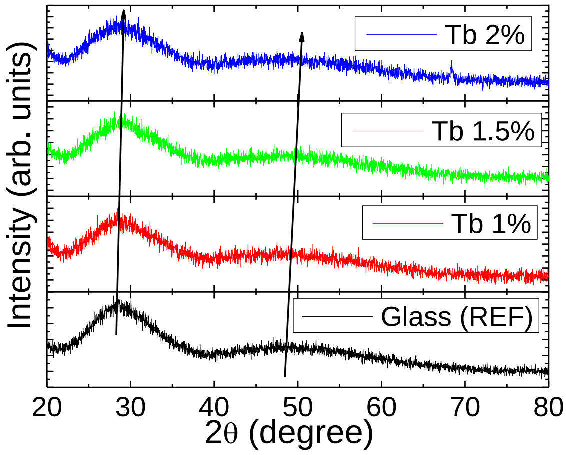

Fig. 1: X-ray diffraction pattern of TeO_2: ZnO: Li_2O: PbO: Wo_3: B_2O_3

4.2 Scanning electron microscopy (SEM)

SEM image explores the smooth surface of the sample. This smooth surface indicates that the amorphous behavior of the glass matrix and also we cannot identified any grain boundaries from the surface morphological image of the host ZLLBTT glass sample as shown in Fig. 2

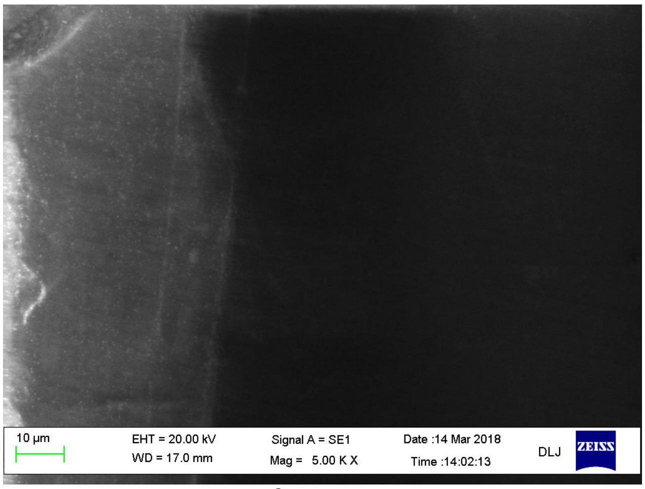

Fig. 2 SEM of Tb^{3+}doped ZLLBTT (01) glass

4.3 Thermal Property

Figure 3 shows the thermal properties of ZLLBTT glass from 300^0C to 1000^0C. From the DSC curve of present glasses system, we can find out that no crystallization peak is apparent and the glass transition temperature T_g are 350,450 and 581 respectively. The T_g increase with the contents of Tb_2O_3 increase. We could conclude that thermal properties of the ZLLBTT glass are good for fiber drawing from the analysis of DSC curve.

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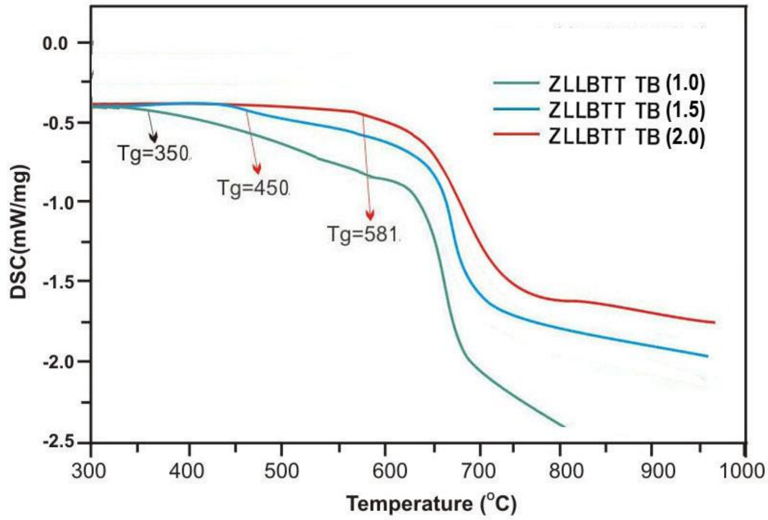

Fig.3: DSC curve of ZLLBTT (TB) glasses.

4.4 Absorption Spectrum

The absorption spectra of Tb^{3+} doped ZLLBTT (TB 01) glass specimen has been presented in Figure 3 in terms of optical density versus wavelength (nm). Five absorption bands have been observed from the ground state $^7F_6$ to excited states $^5D_4$, ($^5D_3$, $^5G_6$), $^5L_{10}$,
($^5D_2$, $^5G_4$, $^5G_5$) and $^5L_9$ for Tb^{3+}doped ZLLBTT glasses.

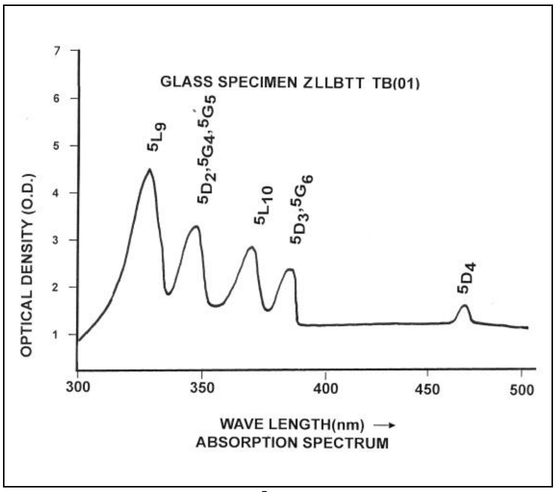

Fig.4: Absorption spectrum of Tb^{3+}doped ZLLBTT (01) glass

The experimental and calculated oscillator strengths for Tb^{3+}ions in zinc lead lithium borotengsten tellurite glasses are given in Table 2.

Table 2: Measured and calculated oscillator strength (P_m×10^{+6}) of Tb^{3+}ions in ZLLBTT glasses.

Energy level from $^7F_6$	**Glass ZLLBT(TB01)**		**Glass ZLLBT(TB1.5)**		**Glass ZLLBT(TB02)**	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^5D_4$	0.57	0.061	0.54	0.070	0.51	0.073
$^5D_3$,$^5G_6$	0.87	0.38	0.84	0.40	0.81	0.42
$^5L_{10}$	1.58	1.14	1.55	1.17	1.52	1.18

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$^5D_2,^5G_4,^5G_5$	1.92	0.57	1.90	0.59	1.87	0.60
$^5L_9$	2.17	0.998	2.14	1.017	2.11	1.032
r.m.s. deviation		0.8829		0.8404		0.8032

Computed values of F_2, Lande's parameter (ξ_{4f}), Nephlauxetic ratio(β') and bonding parameter($b^{1/2}$) for Tb^{3+} doped ZLLBTT glass specimen are given in Table 3.

Table 3. F_2, ξ_{4f}, β' and $b^{1/2}$ parameters for Terbium doped glass specimen

Glass Specimen	F_2	ξ_{4f}	β'	$b^{1/2}$
Tb^{3+}	400.26	1820.87	0.9703	0.1219

In the present case the three Ω_λ parameters follow the trend $\Omega_2 > \Omega_6 > \Omega_4$. The spectroscopic quality factor (Ω_4/Ω_6) related with the rigidity of the glass system has been found to lie between 0.6559 and 0.6607in the present glasses.

The value of Judd-Ofelt intensity parameters are given in Table 4

Table4: Judd-Ofelt intensity parameters for Tb^{3+} doped ZLLBTT glass specimens

Glass Specimen	Ω_2(pm^2)	Ω_4(pm^2)	Ω_6(pm^2)	Ω_4/Ω_6	References
ZLLBTT (TB01)	5.920	1.698	2.578	0.6559	P.W.
ZLLBTT (TB1.5)	7.553	1.602	2.632	0.6087	P.W.
ZLLBTT (TB02)	7.946	1.758	2.661	0.6607	P.W.
BTN (DY)	13.26	2.34	4.01	0.5835	[23]
ZPNT(DY)	5.66	0.84	2.17	0.3871	[24]

The values of Ω_4/Ω_6 for glasses studied are given in Table 4. Tb^{3+} doped ZLLBTT glasses are having larger value of (Ω_4/Ω_6) than [BTN (DY) and ZPNT (DY)].It shows that ZLLBTT (TB) glasses are a kind of better optical glass.

4.5 Fluorescence Spectrum

The fluorescence spectrum of Tb^{3+}doped in Zinc Lead Lithium Borotengsten Tellurite glass is shown in Figure 4. There are four bands observed in the Fluorescence spectrum of Tb^{3+}doped Zinc Lead Lithium Borotengsten Tellurite glass. The wavelengths of these bands along with their assignments are given in Table 5. Fig. (5), Shows the fluorescence spectrum with four peaks ($^5D_4 \rightarrow ^7F_6$), ($^5D_4 \rightarrow ^7F_5$), ($^5D_4 \rightarrow ^7F_4$) and ($^5D_4 \rightarrow ^7F_3$), respectively for glass specimens.

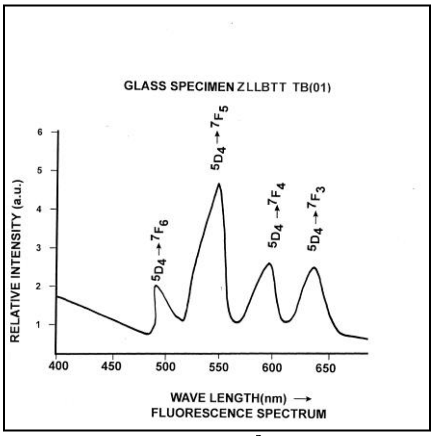

Fig.5: fluorescence spectrum of Tb^{3+}doped ZLLBTT (01) glass

Table 5. Emission peak wave lengths (λ_{max}),radiative transition probability (A_{rad}),branching ratio (β),stimulated emission cross-section(σ_p) and radiative life time(τ_R) for various transitions in Tb^{3+}doped ZLLBTT glasses.

Transition		ZLLBTT TB 01				ZLLBTT TB 1.5				ZLLBTT TB 02			
	λ_{max} (nm)	$A_{rad}(s^{-1})$	β	σ_p (10^{-20} cm^2)	$\tau_R(\mu s)$	$A_{rad}(s^{-1})$	β	σ (10^{-20} cm^2)	$\tau_R(\mu s)$	$A_{rad}(s^{-1})$	β	σ_p (10^{-20} cm^2)	$\tau_R(\mu s)$
$^5D_4 \rightarrow {}^7F_6$	488	2344.66	0.0988	0.3299		2696.25	0.0927	0.3732		2820.40	0.0922	0.3866	
$^5D_4 \rightarrow {}^7F_5$	550	16643.10	0.7012	2.772	42.13	20849.20	0.7169	3.460	34.39	21938.10	0.7172	3.625	32.69
$^5D_4 \rightarrow {}^7F_4$	582	1628.01	0.0686	0.5587		1685.52	0.0580	0.5712		1776.29	0.0581	0.5978	
$^5D_4 \rightarrow {}^7F_3$	625	3119.49	0.1314	0.7600		3851.56	0.1324	0.9314		4052.63	0.1325	0.9762	

5. CONCLUSION

In the present study, the glass samples of composition (35-x) TeO_2: 10ZnO: $10Li_2O$:10PbO: $15Wo_3$:20 B_2O_3: x Tb_2O_3 (where x=1, 1.5, 2mol %) have been prepared by melt-quenching method. Judd-Ofelt intensity parameters Ω_λ (λ=2, 4, 6) are evaluated from the intensities of various absorption bands of optical absorption spectra. The radiative transition probability is highest for ($^5D_4 \rightarrow {}^7F_5$) transition and hence it is useful for laser action. The stimulated emission cross section (σ_p) has highest value for the transition ($^5D_4 \rightarrow {}^7F_5$) in all the glass specimens doped with Tb^{3+} ion. This shows that ($^5D_4 \rightarrow {}^7F_5$) transition is most probable transition.

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