Spectral and Transmittance properties of Tb^{3+} ions doped Zinc Lithium Lead Potassiumniobate Tellurite Glasses

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***Abstract*: Glass of the system: (40-x) TeO_2:10ZnO:10Li_2O:10PbO:10K_2O:20Nb_2O_5: xTb_2O_3. (where x=1, 1.5,2 mol %) have been prepared by melt-quenching method. The amorphous nature of the prepared glass samples was confirmed by X-ray diffraction. Optical absorption, Excitation, fluorescence and Transmittance spectra have been recorded at room temperature for all glass samples. Judd-Ofelt intensity parameters Ω_λ (λ=2, 4 and 6) are evaluated from the intensities of various absorption bands of optical absorption spectra. 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.**

***Keywords*: ZLLPNT glasses, Energy interaction parameters, Optical properties, Transmittance properties.**

I. Introduction

Glass is a continuous random network lacking both symmetry and periodicity. Glasses are super cooled liquid and amorphous in nature. It is obtained by cooling a liquid below its freezing point so quickly that the atoms do not get sufficient time to arrange themselves into an appropriate crystal structure. The classical explanation for the formation of a glass is that when a liquid is cooled, its viscosity increases and at a certain temperature below its freezing point, fluidity becomes almost zero and the liquid becomes rigid. Transparent glass–ceramic as host materials for active optical ions have attracted great interest recently due to their potential application in optical devices such as frequency-conversion materials, lasers and optical fiber amplifiers. The oxide glasses generally possess a good mechanical strength, chemical durability, and thermal stability [1-5]. Tellurite glasses combine the attributes of wide transmission region, good glass stability, rare earth ion solubility, slow corrosion rate, lowest phonon energy spectrum among oxide glass formers, high refractive index, excellent chemical and thermal stability [6-8]. 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]. Tb^{3+} doped glasses are very important because of the possibility of their application in optoelectronic and optic device fields, such as lasers, fiber optic and solar cells [15-17].

The aim of the present study is to prepare the Tb^{3+} doped zinc lithium lead potassiumniobate tellurite glass with different Tb_2O_3 concentrations. The absorption, Excitation, fluorescence and Transmittance 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.

II. Experimental Techniques

Preparation of glasses

The following Tb^{3+} doped Tellurite glass samples (40-x) TeO_2:10ZnO:10Li_2O:10PbO:10K_2O:20Nb_2O_5: 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, ZnO Li_2O, PbO K_2O, Nb_2O_5 and Tb_2O_3. They were thoroughly mixed by using an agate pestle mortar. then melted at 1035^{0}C 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^{0}C 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 %)
ZLLPNT (UD)	40 TeO_2:10ZnO:10Li_2O:10PbO:10K_2O:20Nb_2O_5
ZLLPNT (TB1)	39 TeO_2:10ZnO:10Li_2O:10PbO:10K_2O:20Nb_2O_5:1 Tb_2O_3.
ZLLPNT (TB1.5)	38.5 TeO_2:10ZnO:10Li_2O:10PbO:10K_2O:20Nb_2O_5:1.5 Tb_2O_3.
ZLLPNT (TB 2)	38 TeO_2:10ZnO:10Li_2O:10PbO:10K_2O:20Nb_2O_5:2 Tb_2O_3.

ZLLPNT (UD) -Represents undoped Zinc Lithium Lead Potassiumniobate Tellurite glass specimen.
ZLLPNT (TB) -Represents Tb^{3+} doped Zinc Lithium Lead Potassiumniobate Tellurite glass specimens.

III. Theory

3.1 Oscillator Strength

The spectral intensity is expressed in terms of oscillator strengths using the relation [18].

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

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 [19], 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 [20] and Ofelt [21] 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

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

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:

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

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

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

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

S L J

Where, the sum is over all terminal manifolds.

The radiative life time is given by

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

S L J

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 $\Delta\lambda_{\text{eff}}$ 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 [22, 23]. The Nephelauxetic Ratio is given by

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

Where, ν_g and ν_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

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

IV. Result and Discussion

4.1 XRD Measurement

Figure 1 presents the XRD pattern of the sample contain - TeO_2 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.

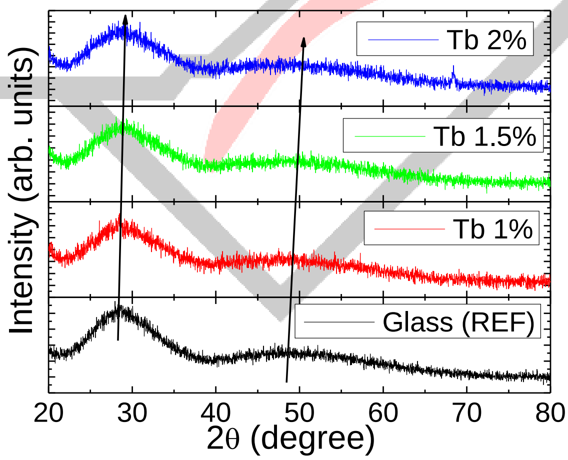

Fig. 1: X-ray diffraction pattern of TeO_2: ZnO: Li_2O: PbO: K_2O: Nb_2O_5

4.2 Transmittance Spectrum

The Transmittance spectrum of Tb^{3+}doped in zinc lithium lead potassiumniobate tellurite glass is shown in Figure 2.

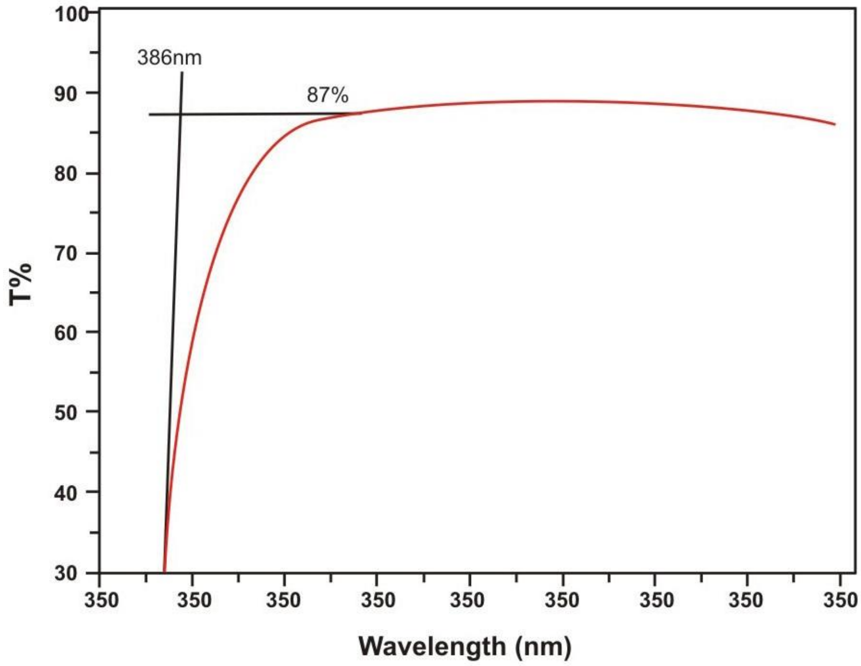

Fig. (2) Transmittance spectrum of Tb^{3+} doped ZLLPNT TB(01) glass.

4.3 Absorption Spectrum

The absorption spectra of Tb^{3+} doped ZLLPNT (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 ZLLPNT(TB 01) glass.

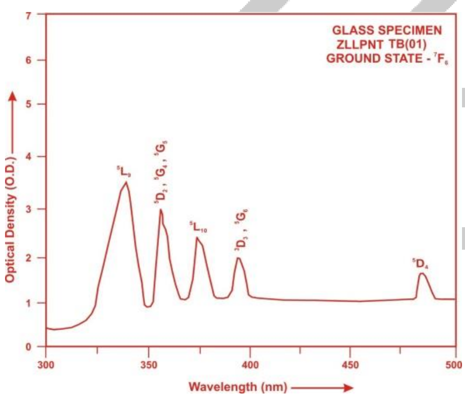

Fig.3: Absorption spectrum of Tb^{3+}doped ZLLPNT TB (01) glass.

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

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

Energy level from $^7F_6$	**Glass ZLLPNT (TB01)**		**Glass ZLLPNT (TB1.5)**		**Glass ZLLPNT (TB02)**	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^5D_4$	0.63	0.048	0.62	0.048	0.60	0.054
$^5D_3$,$^5G_6$	0.95	0.35	0.93	0.34	0.91	0.35
$^5L_{10}$	1.71	1.15	1.70	1.15	1.67	1.16
$^5D_2$,$^5G_4$,$^5G_5$	1.92	0.55	1.90	0.54	1.88	0.55
$^5L_9$	2.22	1.001	2.20	0.997	2.17	1.001
r.m.s. deviation	0.937063		0.924017		0.89395	

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

Table 3. F_2, $\xi_{4f,}$ 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 0.4107 and 0.5384in the present glasses.

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

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

Glass Specimen	**Ω_2(pm²)**	**Ω_4(pm²)**	**Ω_6(pm²)**	**Ω_4/Ω_6**
ZLLPNT (TB01)	4.067	1.437	2.669	0.5384
ZLLPNT (TB1.5)	4.226	1.097	2.671	0.4107
ZLLPNT (TB02)	5.254	1.110	2.680	0.4142

4.4 Excitation Spectrum

The Excitation spectra of Tb^{3+}doped ZLLPNT TB (01) glass specimen has been presented in Figure 4 in terms of Excitation Intensity versus wavelength. The excitation spectrum was recorded in the spectral region 300–550 nm fluorescence at 544nm having different excitation band centered at 305,316, 331, 345, 359,368,377, 386 and 484 nm are attributed to the $^5H_6$, $^5H_7$, $^5D_1$,$^5L_7$+$^5L_8$, $^5L_9$, $^5G_5$, $^5L_{10}$, $^5D_3$+$^5G_6$ and $^5D_4$ transitions, respectively. The highest absorption level is $^5D_3$+$^5G_6$ and is at 386nm.So this is to be chosen for excitation wavelength.

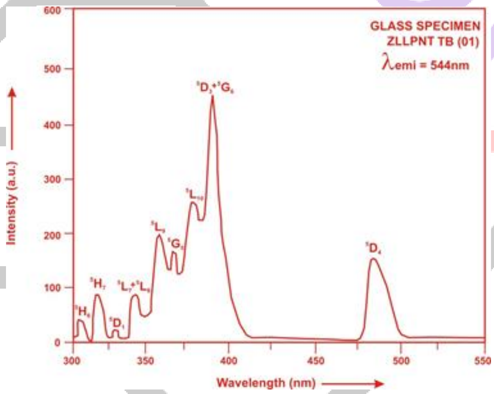

Fig. (4) Excitation spectrum of Tb^{3+}doped ZLLPNT TB (01) glass.

4.5 Fluorescence Spectrum

The fluorescence spectrum of Tb^{3+}doped in zinc lithium lead potassiumniobate tellurite glass is shown in Figure 5. There are four bands observed in the Fluorescence spectrum of Tb^{3+}doped zinc lithium lead potassiumniobate 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.

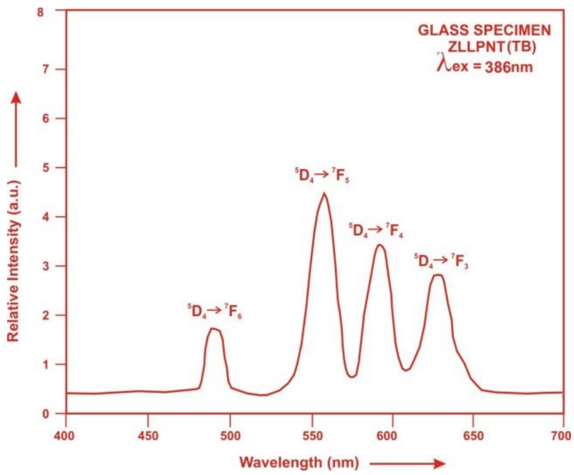

Fig.5: fluorescence spectrum of Tb^{3+}doped ZLLPNT (01) glass

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 ZLLPNTglasses.

Transition		ZLLPNT TB 01				ZLLPNT TB 1.5				ZLLPNT TB 02			
	λ_{max} (nm)	$A_{rad}(s^{-1})$	β	σ_p (10^{-20} cm^2)	τ_R(μs)	$A_{rad}(s^{-1})$	β	σ (10^{-20} cm^2)	τ_R(μs)	$A_{rad}(s^{-1})$	β	σ_p (10^{-20} cm^2)	τ_R(μs)
$^5D_4\rightarrow^7F_6$	488	1803.16	0.1098	0.3007		1778.67	0.1069	0.2947		1991.33	0.1004	0.3301	
$^5D_4\rightarrow^7F_5$	550	11112.10	0.6769	1.9178	60.92	11436.50	0.6874	1.9576	60.11	13934.90	0.7024	2.3568	50.40
$^5D_4\rightarrow^7F_4$	582	1367.97	0.08334	0.5589		1252.16	0.0753	0.5039		1307.80	0.06592	0.5149	
$^5D_4\rightarrow^7F_3$	625	2131.25	0.1298	0.5952		2169.28	0.1304	0.6009		2606.06	0.13135	0.7161	

V. Conclusion

In the present study, the glass samples of composition (40-x) TeO2: 10ZnO: 10Li2O:10PbO: 10K2O:20Nb2O5: x Tb2O3. (where x=1, 1.5, 2mol %) have been prepared by melt-quenching method. Judd-Ofelt intensity parameters Ωλ (λ=2, 4, 6) are evaluated from the intensities of various absorption bands of optical absorption spectra. The radiative transition probability is highest for (5D4→7F5) transition and hence it is useful for laser action. The stimulated emission cross section (σp) has highest value for the transition (5D4→7F5) in all the glass specimens doped with Tb3+ ion. This shows that (5D4→7F5) transition is most probable transition. The obtained results indicated that ZLLPNT (TB) glass should be suitable for laser applications.On the basis of spectrophotometric, transmittance reaches about 87% for all silicate glasses doped with Nd3+ ions.

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