Spectral and FTIR Analysis of Tm³⁺ Doped in Zinc Lithium Tungsten Sodalime Borotellurite Glasses

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Abstract: Glass sample of Zinc Lithium Tungsten Sodalime Borotellurite: (35-x) TeO_2:10ZnO:10Li_2O:10WO_3:10CaO:10Na_2O:15B_2O_3:xTm_2O_3. (where x=1,1.5 and 2 mol%) have been prepared by melt-quenching technique.

The amorphous nature of the prepared glass samples was confirmed by X-ray diffraction. Optical absorption ,fluorescence and FTIR spectra were 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. 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: ZLTSLBT Glasses, Optical Properties, Judd-Ofelt Theory, Rare earth ions.

I. INTRODUCTION

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 [1-5]. Among these hosts, the borotellutite system is attractive due to its superior physical, structural and optical properties [6, 7]. ZnO is a wide band gap semiconductor and has received increasing research interest. It is an important multifunctional material due to its specific chemical, surface and micro structural properties [8]. Tellurite glasses have a low glass transition temperature, low melting temperature and high gain density.

The high gain density in tellurite glasses is due to high solubility of rare earth ions in tellurite network [9-14]. Recently, glass-ceramics containing dysprosium oxides have been found in applications for several different purposes. Tm^{3+} doped glasses have attracted much interest due to their important optical properties used in lasers, optical amplifiers, network formers, photonic devices and as infrared sensors [15-18].

The present work reports on the preparation and characterization of rare earth doped heavy metal oxide (HMO) glass systems for lasing materials. I have studied on the absorption, emission and FTIR properties of Tm^{3+} doped zinc lithium tungsten sodalime borotellurite glasses.

The intensities of the transitions for the rare earth ions have been estimated successfully using the Judd-Ofelt theory, The laser parameters such as radiative probabilities(A),branching ratio (β), radiative life time(τ_R) and stimulated emission cross section(σ_p) are evaluated using J.O.intensity parameters(Ω_λ, λ=2,4 and 6).

II. EXPERIMENTAL TECHNIQUES

A. Preparation of Glasses

The following Tm^{3+}doped borotellurite glass samples (35-x) TeO_2:10ZnO:10Li_2O:10WO_3:10CaO:10Na_2O:15B_2O_3:xTm_2O_3. (where x=1,1.5 and 2 mol%) have been prepared by melt-quenching method. Analytical reagent grade chemical used in the present study consist of TeO_2, ZnO, Li_2O, WO_3, CaO, Na_2O_3,B_2O_3 and Tm_2O_3.

They were thoroughly mixed by using an agate pestle mortar. then melted at 980^0C 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 250^0C 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 %)
ZLTSLBT (UD)	$35TeO_2:10ZnO:10Li_2O:10WO_3:10CaO:10Na_2O:15B_2O_3$
ZLTSLBT (TM1)	$34TeO_2:10ZnO:10Li_2O:10WO_3:10CaO:10Na_2O:15B_2O_3:1Tm_2O_3$
ZLTSLBT (TM1.5)	$33.5TeO_2:10ZnO:10Li_2O:10WO_3:10CaO:10Na_2O:15B_2O_3:1.5Tm_2O_3$
ZLTSLBT (TM 2)	$33TeO_2:10ZnO:10Li_2O:10WO_3:10CaO:10Na_2O:15B_2O_3:2 Tm_2O_3$

ZLTSLBT (UD) -Represents undoped Zinc Lithium Tungsten Sodalime Borotellurite
glass specimen.

ZLTSLBT (TM) -Represents Tm^{3+} doped Zinc Lithium Tungsten Sodalime Borotellurite
glass specimens.

III. THEORY

A. Oscillator Strength

The intensity of spectral lines are expressed in terms of oscillator strengths using the relation [19].

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

where, $\varepsilon (v)$ 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 [20], using the modified relation:

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

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

B. Judd-Ofelt Intensity Parameters

According to Judd [21] and Ofelt [22] 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:

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

$$(3)$$

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

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

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=2,4and 6) are known as Judd-Ofelt intensity parameters.

C. 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:

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

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 $\mid 4f^N$ (S', L') J'> to a final many fold $\mid 4f^N$ (S, L) J > is given by

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

S L J

where, the sum is over all terminal manifolds.

The radiative life time is given by

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots_{rad}\,\cdots\cdots\ A[(S', L')\,J';\,(S,L)\,] = A_{Total}^{-1}$$

(7)

S L J

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

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

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

IV.   RESULT AND DISCUSSION

A.   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
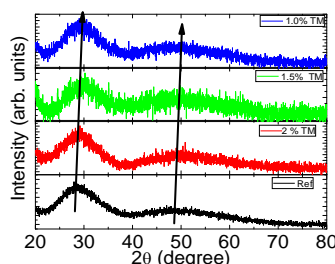

Fig. 1 X-ray diffraction pattern of TeO_2:ZnO:Li_2O:WO_3:CaO:Na_2O:B_2O_3: Tm_2O_3.

B.   FTIR Transmission Spectrum

The FTIR spectrum of ZLTSLBT TM (01) glass is in the wave number range400-1600 cm^{-1} is presented in Fig.2 and the possible mechanism bands are tabulated in Table 2.
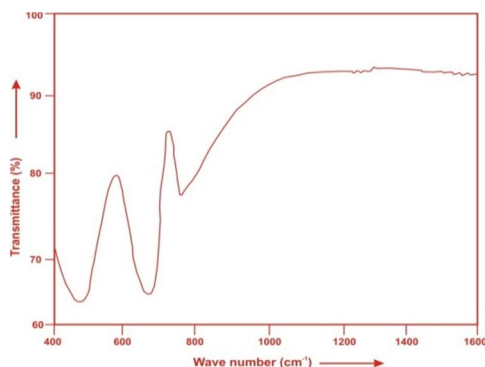

Fig. (2) FTIR spectrum of ZLTSLBT TM (01) glass.

In the studied glasses, the absorption band at 426 cm^{-1} is appeared due to the symmetric stretching vibration of the Zn-O bond [23].whereas the band at 680 cm^{-1} is due to the stretching vibrations of Te–O bonds in trigonal bipyramidal units TeO$_4$ (tbp) [24]. The band at 771 cm-1 is evolved for pure and doped glasses due to trigonal pyramidal structural units. This band is attributed to the stretching vibration within the tellurium and the non-bridging oxygen of trigonal pyramidal structure [25].

Table2. Assignment of infrared transmission bands of (ZLTSLBT TM 01) glass.

Peak position(cm^{-1})	Band Assignment
~ 465	symmetric stretching vibration of the Zn-O bond [23]
~680	stretching vibrations of Te–O bonds in trigonal bipyramidal units TeO$_4$[24]
~771	trigonal pyramidal structural units [25]

C. Absorption Spectrum

The absorption spectra of Tm^{3+}doped ZLTSLBT glass specimens have been presented in Figure 3 in terms of optical density versus wavelength. Five absorption bands have been observed from the ground state $^3H_6$ to excited states $^3F_4$, $^3H_5$, $^3H_4$, $^3F_3$ and $^1G_4$ for Tm^{3+} doped ZLTSLBT glasses.
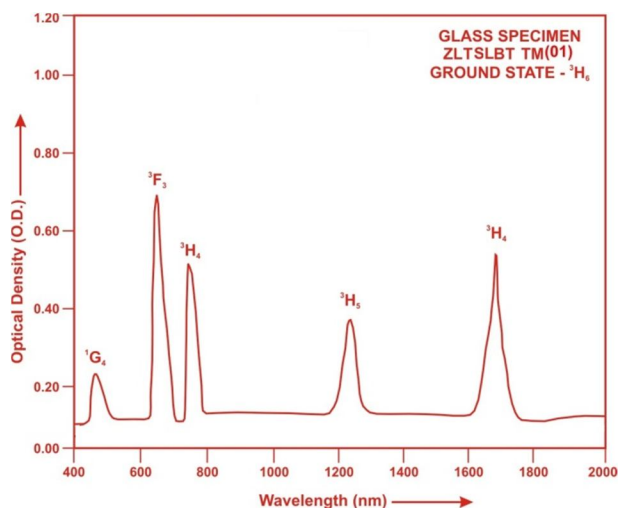

Fig. (3) Absorption spectrum of ZLSLBT TM (01) glass.

The experimental and calculated oscillator strength for Tm^{3+} ions in ZLTSLBT glasses are given in **Table 3.**

Table 3: Measured and calculated oscillator strength (P$_m$×10^{+6}) of Tm^{3+}ions in ZLTSLBT glasses.

Energy level from $^3H_6$	Glass ZLTSLBT (TM01)		Glass ZLTSLBT (TM1.5)		Glass ZLTSLBT (TM02)	
	P$_{exp.}$	P$_{cal.}$	P$_{exp.}$	P$_{cal.}$	P$_{exp.}$	P$_{cal.}$
$^3F_4$	1.80	1.85	1.77	1.83	1.74	1.81
$^3H_5$	1.36	1.45	1.32	1.44	1.30	1.43
$^3H_4$	1.96	2.06	1.93	2.05	1.90	2.04
$^3F_3$	2.92	3.03	2.89	3.02	2.84	2.99
$^1G_4$	0.71	0.89	0.67	0.89	0.63	0.89
r.m.s. deviation	±0.11663		±0.14050		±0.16291	

In the Zinc Lithium Tungsten Sodalime Borotellurite glasses (ZLTSLBT) Ω_2, Ω_4 and Ω_6 parameters decrease with the increase of x from 1 to 2 mol%. The order of magnitude of Judd-Ofelt intensity parameters is $\Omega_4>\Omega_2>\Omega_6$ for all the glass specimens. The spectroscopic quality factor (Ω_4/Ω_6) related with the rigidity of the glass system has been found to lie between 1.401 and 1.439 in the present glasses.

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

Table 4: Judd-Ofelt intensity parameters for Tm^{3+} doped ZLTSLBT glass specimens

Glass Specimen	$\Omega_2(pm^2)$	$\Omega_4(pm^2)$	$\Omega_6(pm^2)$	Ω_4/Ω_6
ZLTSLBT (TM 01)	6.367	7.733	5.373	1.439
ZLTSLBT (TM 1.5)	6.276	7.649	5.359	1.427
ZLTSLBT (TM 02)	6.268	7.489	5.347	1.401

D. Fluorescence Spectrum

The fluorescence spectrum of Tm^{3+} doped in glass is shown in Figure 4. There are nine broad bands observed in the Fluorescence spectrum of Tm^{3+} doped zinc lithium tungsten sodalime borotellurite glass. The wavelengths of these bands along with their assignments are given in Table 5. The peak with maximum emission intensity appears at 1810 nm and corresponds to the ($^3F_4 \rightarrow ^3H_6$) transition.
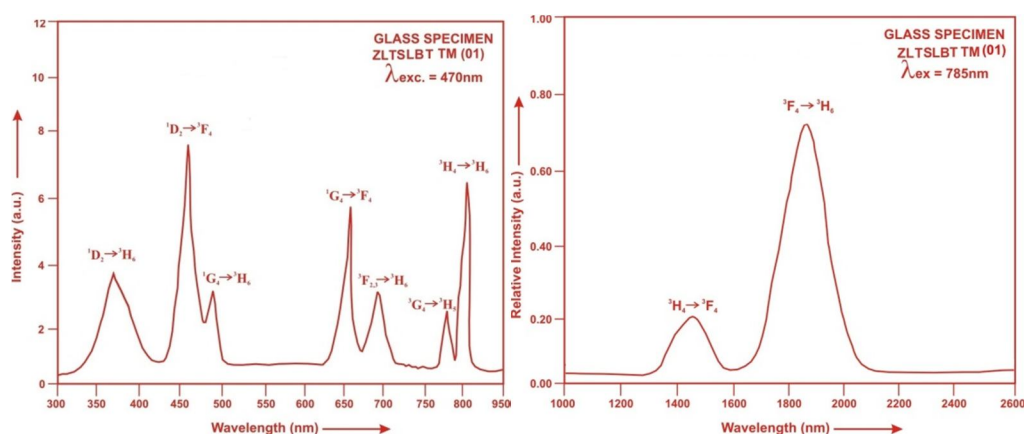

Fig. (4). Fluorescence spectrum of ZLSLBT TM (01) glass.

Table5: Emission peak wave lengths (λ_p),radiative transition probability (A_{rad}),branching ratio (β),stimulated emission cross-section(σ_p) and radiative life time(τ_R)for various transitions in Tm^{3+} doped ZLTSLBT glasses

Transition	ZLTSLBT (TM 01)					ZLTSLBT (TM 1.5)				ZLTSLBT (TM 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_p $(10^{-20}$ $cm^2)$	$\tau_R (\mu s)$	$A_{rad}(s^{-1})$	β	σ_p $(10^{-20}$ $cm^2)$	τ_R $(10^{-20}$ $cm^2)$
$^1D_2\rightarrow^3H_6$	365	59863.50	0.6277	1.482		59484.40	0.6281	1.516		58663.10	0.6258	1.558	
$^1D_2\rightarrow^3F_4$	455	19680.30	0.2064	2.302		19466.80	0.2056	2.462		19416.00	0.2071	2.656	
$^1G_4\rightarrow^3H_6$	480	2476.11	0.0259	0.548		2452.76	0.0259	0.576		2425.11	0.0259	0.628	
$^1G_4\rightarrow^3F_4$	651	812.57	0.0085	1.478		809.74	0.0086	1.627	10.5594	805.60	0.0086	2.362	10.668
$^3F_{2,3}\rightarrow^3H_6$	689	6143.18	0.0644	2.309	10.4853	6121.39	0.0646	2.422		6080.14	0.0648	2.485	
$^1G_4\rightarrow^3H_5$	785	2369.10	0.0248	2.453		2363.50	0.0250	2.630		2361.71	0.0252	2.800	
$^3H_4\rightarrow^3H_6$	798	3128.37	0.0328	4.319		3112.41	0.0329	4.748		3104.71	0.0331	5.239	
$^3H_4\rightarrow^3F_4$	1450	398.35	0.0042	3.745		395.66	0.0042	3.831		393.13	0.0042	3.987	
$^3F_4\rightarrow^3H_6$	1810	500.30	0.0052	7.138		495.77	0.0052	7.200		490.79	0.0052	7.306	

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V. CONCLUSION

In the present study, the glass samples of composition $(35-x)TeO_2:10ZnO:10Li_2O:10WO_3:10CaO:10Na_2O:15B_2O_3$:xTm_2O_3 (where x =1, 1.5 and 2mol %) have been prepared by melt-quenching method. The value of stimulated emission cross-section (σ_p) is found to be maximum for the transition ($^3F_4 \rightarrow {}^3H_6$) for glass ZLTSLBT (TM 01), suggesting that glass ZLTSLBT (TM 01) is better compared to the other two glass systems ZLTSLBT (TM 1.5) and ZLTSLBT (TM 02).

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