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Spectral and Thermal Properties of Tm^{3+} Doped in Zinc Lithium Alumino Tungsten Borozirconate Glasses

S.L.Meena

CeramicLaboratory, Department of physics,
Jai NarainVyas University, Jodhpur 342001(Raj.) India
E-mail address:shankardiya7@rediffmail.com

Abstract

Glass of the system: $(35-x)\ ZrO_2:10ZnO:10Li_2O:10Al_2O_3:15WO_3:20B_2O_3:\ xTm_2O_{3.}$ (where x=1, 1.5,2 mol %) have been prepared by melt-quenching method. (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 and fluorescence spectra were recorded at room temperature for all glass samples. Judd-ofelt intensity parameters Ω_λ (λ=2, 4 and6) are evaluated from the intensities of various absorption bands of optical absorption spectra. Using these intensity parameters various radiative properties like spontaneous emission probability (A), branching ratio(β), radiative life time (τ_R), stimulated emission cross–section (σ_p)of various emission lines and Thermal parameters have been evaluated.

Keywords: ZLATBZ Glasses, Optical Properties, Judd-ofelt Theory, Laser Parameters Thermal parameters.

I. Introduction

Rare earth glasses have attracted much attention, becausethey have large practical and potential applications in manyfields, such as glass lasers, optical fiber amplifiers, phosphors,electro-luminescent devices, memory devices andflat-panel displays [1–5].The zirconate glasses offer good laser and optical properties such as high refractive index, high cross-section for stimulated emission and thermo-mechanical properties. Moreover, these properties can be improved by chemical strengthening [6, 7].Among active rare-earth ions Pm^{3+} exhibits high solubility in zirconateglasses, which also possess excellent physiochemical properties.ZLATBZ is a model material that is being developed for many photonic applications.B_2O_3 is one of the most common glass former oxides and is present in almost all commercially important glasses. It is often used as a dielectric and insulating material [8].Due to their good chemical durability, erbium-doped soda-lime silicate glasses are attractive materials for the fabrication of low-cost integrated optical amplifiers by using the ion-exchange technique. Zirconate Glasses are both scientifically and technologically important materials because they generally offer some unique physical properties better than other Glasses [9-13]. Zirconate glass exhibit very important physical properties such as low melting temperature, low glass transition temperature and low softening temperature.

The present work reports on the preparation and characterization of rare earth doped heavy metal oxide (HMO) glass systems for lasing materials. We have studied on the absorption and emission properties of Tm^{3+}doped zinc lithium alumino tungsten borozirconate glasses. The intensities of the transitions for the rare earth ions have been estimated successfully using the Judd-Ofelttheory. The laser parameters such as radiative probabilities (A),branching ratio (β), radiative life time(τ_R), stimulated emission cross section(σ_p)and Thermal parameters have been evaluated.

II.Experimental Techniques

Preparation of glasses

The following Tm^{3+}doped borozirconateglass samples (35-x) ZrO_2:10ZnO:10Li_2O:10 Al_2O_3:15WO_3:20B_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 ZrO_2,ZnO,Li_2O, Al_2O_3, WO_3,$B_2O_3$and Tm_2O_3. They were thoroughly mixed by using an agate pestle mortar. then melted at 950^0C 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 %)
ZLATBZ (UD)	$35ZrO_2:10ZnO:10Li_2O:10Al_2O_3:15WO_3:20B_2O_3$.
ZLATBZ(TM 1)	$34\ ZrO_2:10ZnO:10Li_2O:10Al_2O_3:15WO_3:20B_2O_3:1Tm_2O_3$
ZLATBZ(TM 1.5)	$33.5\ ZrO_2:10ZnO:10Li_2O:10Al_2O_3:15WO_3:20B_2O_3:1.5Tm_2O_3$
ZLATBZ(TM 2)	$33\ ZrO_2:10ZnO:10Li_2O:10Al_2O_3:15WO_3:20B_2O_3:2Tm_2O_3$

ZLATBZ (UD) -Represents undopedzinc lithium alumino tungsten borozirconate glass specimens.

ZLATBZ (TM) -Represents Tm^{3+}dopedzinc lithium alumino tungsten borozirconate glass specimens.

III.Theory

3.1Oscillator Strength

The intensity of spectral lines are expressed in terms of oscillator strengths using the relation [14].

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

where, $\varepsilon(\nu)$ 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 [15], using the modified relation:

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

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 $\Delta\upsilon_{1/2}$is half band width.

3.2. Judd-Ofelt Intensity Parameters

According to Judd[16] and Ofelt[17] 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

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

$\lambda = 2, 4, 6$

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.

3.3Radiative 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:

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

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

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

S L J

where, the sum is over all terminal manifolds.

The radiative life time is given by

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

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

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

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

4.1XRD Measurement

Figure 1 presents the XRD pattern of the sample contain –ZrO_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.

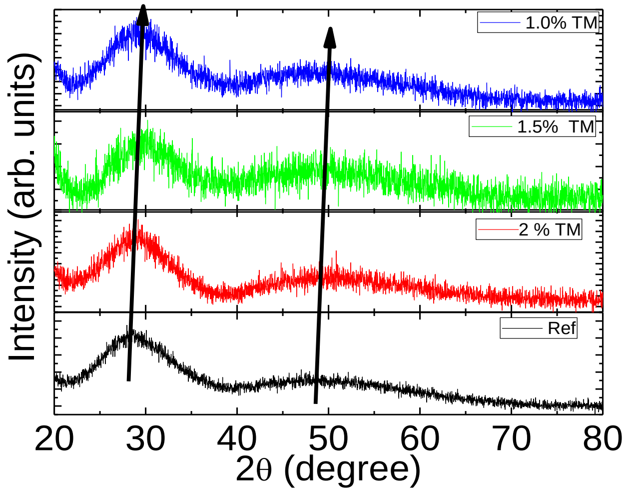

Fig. 1 X-ray diffraction pattern of ZrO_2:ZnO: Li_2O:Al_2O_3:WO_3:B_2O_3: Tm_2O_3.

4.2. Thermal Studies

Fig. 2 depicts the DTA thermogram of powdered ZLATBZ sample show an endothermic peak corresponding to glass transition event followed by an exothermic peak related to crystallization event. The glass transition temperature (T_g), onset crystallization temperature (T_x), crystallization temperature (T_c) were estimated to be 516^0C, 585^0C and 613^0C respectively. From the measured value of T_g,$T_x$and T_c , the glass stability factor ($\Delta T = T_x - T_g$) has been determined to be 69^0C indicating the good stability of the glass . Therefore, the present glass composition could also be used to draw fiber and used to determine the required heat temperatures applied to induce crystallization.

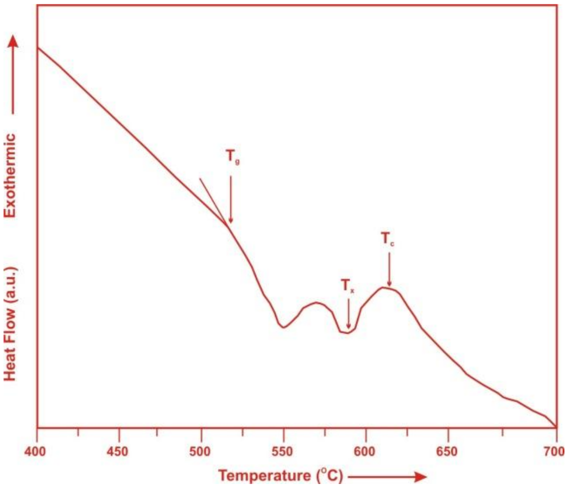

Fig. 2. DTA thermogram of powdered ZLATBZ sample.

Obtained results indicate that by increasing the amount of mol% Tm_2O_3, the $T_g$of thesamples also increases, the small increase of $T_g$in these glasses shows that the structure is strongly and progressively modified.The thermal stabilities $\Delta T$of theZLATBZreference glass and Tm^{+3}doped ZLATBZ glass has been evaluated from their T_g, $T_c$and $T_c$values, the resultsare listed out in Table 2.Hruby's parameter also calculated by using eq. (9), the greater values of the Hruby's parameter indicate higher glass forming tendency, the values of Hin our glasses increased with the addition of the Tm_2O_3.Eqs. (10) and (11) present the GS parameter ofWeinberg[20]and Lu and Liu [21], respectively.

$$H=\frac{T_X-T_g}{T_c-T_X} \quad (9)$$

$$K_W=\frac{T_X-T_g}{T_c} \quad (10)$$

$$K_{LL}=\frac{T_X}{T_g+T_c} \quad ..... (11)$$

Table 2: Thermal parameters determined from the DTA traces of ZLATBZ(TM) glasses.

Sample Name	% Tm_2O_3	T_g ^{0}C	T_X ^{0}C	T_C ^{0}C	ΔT	H	K_W	K_{LL}
ZLATBZ (TM 1.0)	1	516	585	613	69	2.46	0.1126	0.5182
ZLATBZ (TM 1.5)	1.5	518	588	615	70	2.59	0.1138	0.5190
ZLATBZ (TM 02)	2	522	593	618	71	2.84	0.1149	0.5202

4.3 Absorption Spectrum

The absorption spectra of Tm^{3+}doped ZLATBZ 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 ZLATBZglasses.

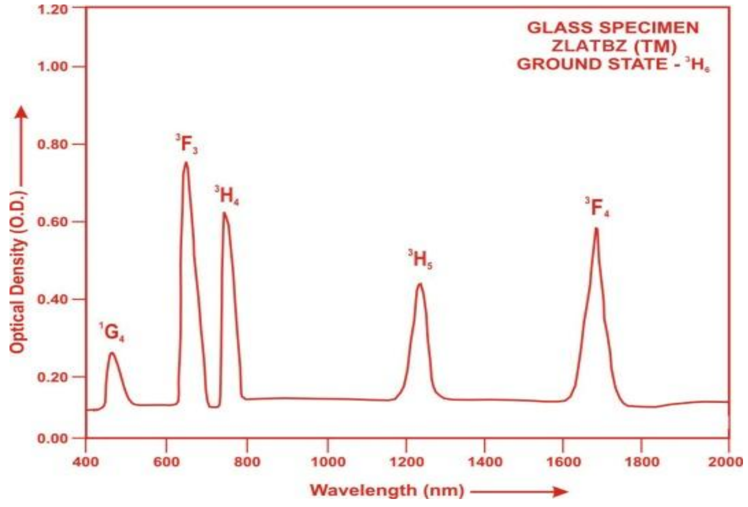

Fig. (3) Absorption spectrum of Tm^{3+}doped ZLATBZglasses

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

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

Energy level from $^3H_6$	**Glass ZLATBZ(TM01)**		**Glass ZLATBZ(TM1.5)**		**Glass ZLATBZ(TM02)**	
	P_{exp}.	P_{cal}.	P_{exp}.	P_{cal}.	P_{exp}.	P_{cal}.
$^3F_4$	1.82	1.87	1.80	1.85	1.77	1.83
$^3H_5$	1.38	1.46	1.35	1.44	1.33	1.44
$^3H_4$	1.95	2.046	1.93	2.029	1.90	2.02
$^3F_3$	2.96	3.07	2.93	3.037	2.91	3.037
$^1G_4$	0.73	0.90	0.71	0.89	0.68	0.89
r.m.s. deviation	±0.1056		±0.1133		±0.1331	

In theZincLithiumAluminoTungstenBorozirconateglasses (ZLATBZ)Ω_2, Ω_4 and $\Omega_6$parameters decrease with the increase of x from 1 to 2 mol%. The order ofmagnitude 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 1.4925 and 1.5095 in the present glasses.

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

Table4:Judd-Ofelt intensity parameters for Tm^{3+} doped ZLATBZglass specimens.

Glass Specimen	**Ω_2(pm^2)**	**Ω_4(pm^2)**	**Ω_6(pm^2)**	**Ω_4 /Ω_6**
ZLATBZ (TM 01)	6.155	8.130	5.386	1.5095
ZLATBZ(TM 1.5)	6.118	8.038	5.335	1.5067
ZLATBZ (TM 02)	5.951	7.982	5.348	1.4925

4.4. Fluorescence Spectrum

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

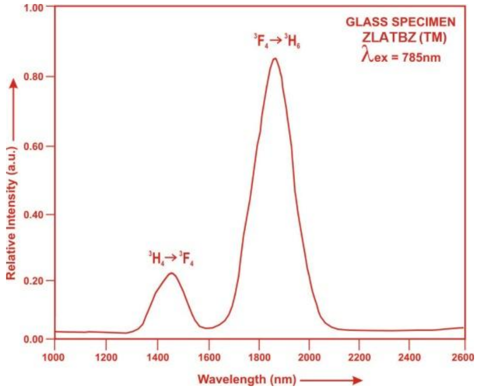

Fig. (4). Fluorescence spectrum of doped with Tm^{3+}ZLATBZglasses.

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 ZLATBZ glasses

Transition		ZLATBZ(TM01)				ZLATBZ(TM1.5)				ZLATBZ(TM 02)			
	λ_{emi} (nm)	$A_{rad}(s^{-1})$	β	$\sigma_p(10^{-20}$ cm^2)	$\tau_R(10^{-20}$ cm^2)	$A_{rad}(s^{-1})$	β	$\sigma_p(10^{-20}$ cm^2)	$\tau_R(10^{-20}$ cm^2)	$A_{rad}(s^{-1})$	β	$\sigma_p(10^{-20}$ cm^2)	$\tau_R(10^{-20}$ cm^2)
$^3H_4 \rightarrow {}^3F_4$	1450	393.49	0.4414	4.834	1121.75	390.55	0.4414	4.615	1130.10	387.82	0.4422	4.440	1140.28
$^3F_4 \rightarrow {}^3H_6$	1810	498.98	0.5586	6.468		494.33	0.5586	6.306		489.16	0.5578	6.132	

V. Conclusion

In the present study, the glass samples of composition (35-x) ZrO2:10ZnO:10Li2O:10Al2O3:15WO3:20B2O3.

xTm2O3. (where x =1, 1.5 and 2mol %) have been prepared by melt-quenching method. The value of stimulated emission cross-section (σp) is found to be maximum for the transition (3F4→3H6) for glass ZLATBZ (TM 01), suggesting that glass ZLATBZ (TM 01) is better compared to the other two glass systems ZLATBZ (TM 1.5) and ZLATBZ (TM 02)., the values of Hruby's parameter (H)in my glasses increased with the addition of the Tm2O3.

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