Spectroscopic Properties of Tb^{3+} Doped in Yttrium Zinc Lithium Bismuth Borate Glasses

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Abstract

Glass sample of Yttrium Zinc Lithium Bismuth Borate (20-x) Bi_2O_3:15Li_2O:15ZnO: 10Y_2O_3:40 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 yttrium zinc lithium bismuth borate glasses have been recorded at room temperature. The various interaction parameters like Slater-Condon parameters F_K (k=2,4,6), 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 and laser parameters have also been calculated.

Keywords: Bismuth borate glasses, Energy interaction parameters, Optical properties, Judd-Ofelt analysis.

Introduction

Bismuth borate glasses is of great interest because of their applications as optical fiber amplifiers, optoelectronics, magneto optical devices, laser material, thermal and mechanical sensors, electro-optic switches, solid state laser materials, photonic switches and reflecting windows[1-4]. These bismuth borate glasses are also having the important properties such as high refractive index, extensive glass formation range, high physical and chemical stability, low melting temperature, long infrared cut off and high infrared transparency. In order to improve the glass quality and its optical performance a divalent oxide such as ZnO has been added separately beside the other property improving network modifier (NWF) namely Li_2O.

Bismuth borate glasses have lesser degree of amplified spontaneous emission losses. They can be used either in large bulk devices like single power tetrawatt lasers in a nanosecond pulse for thermonuclear fussion or in optical wave guides, to confine the pumping light with high density over a long interaction length. Consequently, rare earth doped glasses are important materials for bulk lasers [5, 6].

The aim of the present study is to prepare the Tb^{3+} doped yttrium zinc lithium bismuth borate 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. Ω_2 parameter is generally related to covalent bonding while Ω_6 to the rigidity of the host.

Experimental Techniques

Preparation of glasses

The following Tb^{3+} doped bismuth borate glass samples (20-x) Bi_2O_3:15Li_2O:15ZnO: 10Y_2O_3:40 B_2O_3: xTb_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 Bi_2O_3, Li_2O, ZnO, Y_2O_3 and $B_2O_3$and Tb_2O_3. They were thoroughly mixed by using an agate pestle mortar. then melted at 1080^0C 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 370^0C 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 %)
YZnLiBiB (UD)	20 Bi_2O_3:15Li_2O:15ZnO: 10 Y_2O_3: 40 B_2O_3
YZnLiBiB (TB1)	19 Bi_2O_3:15Li_2O:15ZnO: 10Y_2O_3:40 B_2O_3: 1Tb_2O_3
YZnLiBiB (TB 1.5)	18.5Bi_2O_3:15Li_2O:15ZnO: 10Y_2O_3:40 B_2O_3: 1.5Tb_2O_3
YZnLiBiB (TB 2)	18 Bi_2O_3:15Li_2O:15ZnO: 10Y_2O_3:40 B_2O_3: 2Tb_2O_3

YZnLiBiB (UD) -Represents undoped Yttrium Zinc Lithium Bismuth Borate glass specimen.
YZnLiBiB (TB) -Represents Tb^{3+} doped Yttrium Zinc Lithium Bismuth Borate glass specimens

Oscillator Strength

The spectral intensity is expressed in terms of oscillator strengths using the relation [7].

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

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 [8], 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.

Judd-Ofelt Intensity Parameters

According to Judd [9] and Ofelt [10] 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

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

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 which contain the effect of the odd-symmetry crystal field terms, radial integrals and energy denominators. $\|U^{(\lambda)}\|^2$ are the matrix elements of the doubly reduced unit tensor operator calculated in intermediate coupling approximation. Ω_λ parameter can be obtained from least square fitting method [11] (Table 4). The matrix element $\|U^{(\lambda)}\|^2$ that are insensitive to the environment of rare earth ions were taken from the literature [12].

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:

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

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

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

Where, the sum is over all terminal manifolds.

The radiative life time is given by

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

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

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

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

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 [13, 14]. The Nephelauxetic Ratio is given by

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

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 ($b^{1/2}$) are given by

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

Result and Discussion

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.

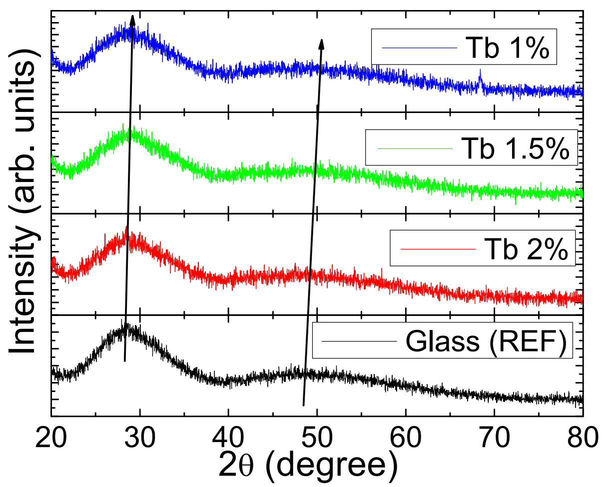

Fig. 1: X-ray diffraction pattern of Bi_2O_3: Li_2O: ZnO: Y_2O_3: B_2O_3: Tb_2O_3

Thermal Property

Figure 1 shows the thermal properties of YZnLiBiB 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 350,454,582 respectively. The T_g increase with the contents of Tb_2O_3 increase. We could conclude that thermal properties of the YZnLiBiB glass are good for fiber drawing from the analysis of DSC curve.

Absorption Spectrum

The absorption spectra of Tb^{3+} doped YZnLiBiB (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 YZnLiBiB glasses.

The experimental and calculated oscillator strengths for Tb^{3+} ions in yttrium zinc lithium bismuth borate glasses are given in Table 2

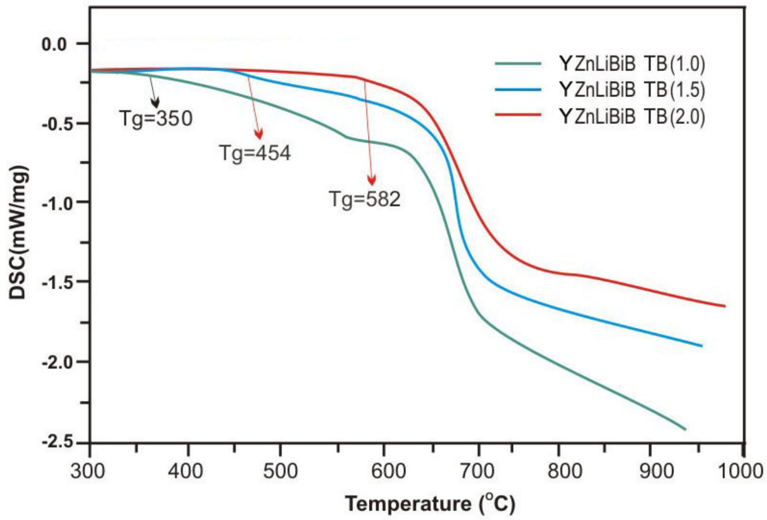

Fig.2: DSC curve of YZnLiBiB (TB) glasses.

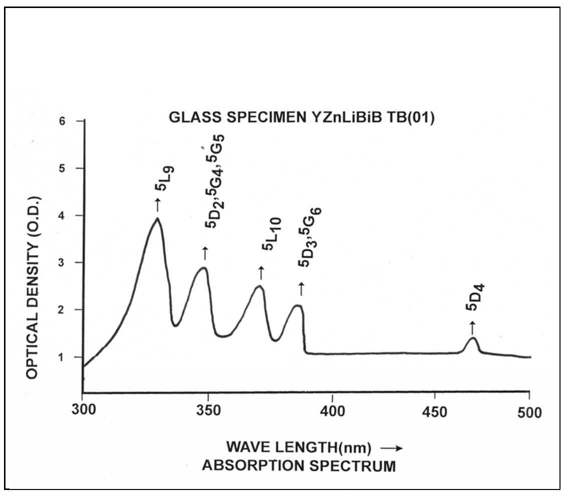

Fig.3: Absorption spectrum of Tb^{3+}doped YZnLiBiB (01) glass

Table2: Measured and calculated oscillator strength ($P_m \times 10^{+6}$) of Tb^{3+}ions in YZnLiBiB glasses.

Energy level from $^7F_6$	Glass YZnLiBiB(TB01)		Glass YZnLiBiB(TB1.5)		Glass YZnLiBiB(TB02)	
	P_{exp}.	P_{cal}.	P_{exp}.	P_{cal}.	P_{exp}.	P_{cal}.
$^5D_4$	0.46	0.076	0.45	0.074	0.44	0.080
$^5D_3$,$^5G_6$	0.83	0.49	0.82	0.50	0.80	0.50
$^5L_{10}$	1.52	1.23	1.50	1.23	1.49	1.24
$^5D_2$,$^5G_4$,$^5G_5$	1.80	0.65	1.79	0.64	1.78	0.65
$^5L_9$	2.09	1.11	2.08	1.11	2.06	1.11
r.m.s.	±0.724		±0.717		±0.700	

deviation						

Computed values of F_2, Lande' parameter (ξ_{4f}), Nephlauxetic ratio(β') and bonding parameter($b^{1/2}$) for Tb^{3+} doped YZnLiBiB 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

Judd-Ofelt intensity parameters Ω_λ (λ=2, 4, 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 $\Omega_2 > \Omega_4 > \Omega_6$. The spectroscopic quality factor (Ω_4 /Ω_6) related with the rigidity of the glass system has been found to lie between 1.456 and 1.682 in the present glasses.

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

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

Glass Specimen	$\Omega_2(pm^2)$	$\Omega_4(pm^2)$	$\Omega_6(pm^2)$	Ω_4 /Ω_6	References
YZnLiBiB(TB01)	5.374	3.749	2.401	1.561	P.W.
YZnLiBiB(TB1.5)	4.903	4.002	2.380	1.682	P.W.
YZnLiBiB(TB02)	6.115	3.499	2.403	1.456	P.W.
YZnLiBiB(ND)	3.574	5.511	4.464	1.235	[15]
YZnLiBiB(SM)	4.080	3.810	3.517	1.083	[16]
BiBS(ND)	3.52	4.19	3.86	1.085	[17]
LBMPN(ND)	4.813	3.170	4.100	0.773	[18]

The values of Ω_4 /Ω_6 for glasses studied are given in Table4. Tb^{3+} doped YZnLiBiB glasses are having larger value of (Ω_4 /Ω_6) than [YZnLiBiB (ND), YZnLiBiB(SM),BiBS(ND) and LBMPN(ND)].It show that YZnLiBiB(TB) glasses is a kind of better optical glass.

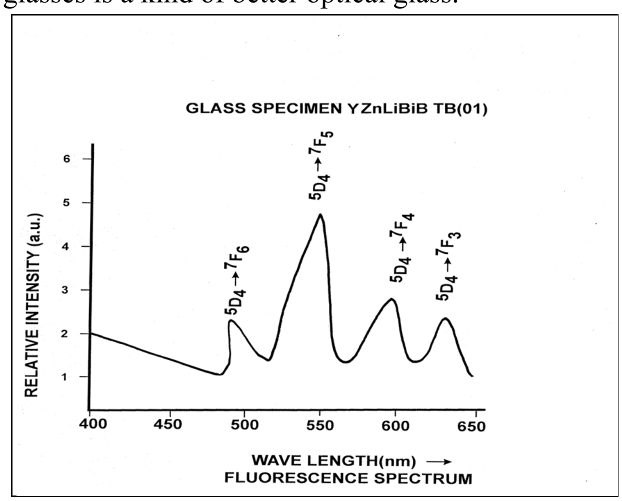

Fig.4: fluorescence spectrum of Tb^{3+}doped YZnLiBiB (01) glass

Fluorescence Spectrum

The fluorescence spectrum of Tb^{3+}doped in yttrium zinc lithium bismuth borate glass is shown in Figure 4. There are four broad bands observed in the Fluorescence spectrum of Tb^{3+}doped yttrium zinc lithium bismuth borate glass. The wavelengths of these bands along with their assignments are given in Table 5. Fig. (4).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.

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 YZnLiBiB glasses

Transition		YZnLiBiB TB 01				Y ZnLiBiBTB 1.5				YZnLiBiBTB 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	3604.690	0.1083	0.4879	30.053	3531.494	0.1122	0.4714	31.764	3778.024	0.1035	0.5015	27.382
$^5D_4\rightarrow{}^7F_5$	550	22039.382	0.6623	3.055		20461.81	0.6499	2.8239		24733.68	0.6773	3.3855	
$^5D_4\rightarrow{}^7F_4$	582	3320.866	0.0998	1.0976		3432.061	0.1090	1.1160		3247.561	0.0889	1.0485	
$^5D_4\rightarrow{}^7F_3$	625	4309.715	0.1295	0.9664		4057.250	0.1289	0.8906		4760.990	0.1304	1.0540	

Conclusion

In the present study, the glass samples of composition (20-x) Bi_2O_3:15Li_2O:15ZnO: 10Y_2O_3: 40 B_2O_3: x Tb_2O_3 (where x=1, 1.5, 2mol %) have been prepared by melt-quenching method. Low r.m.s. deviation values clearly indicate the accuracy of fitting. The Judd-Ofelt theory has been applied to calculate the oscillator strength and intensity parameters Ω_λ (λ=2, 4, 6). 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 useful for laser action.

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