Spectral and Thermal Properties of Tb^{3+} Doped in Lead Lithium Borophosphate Glasses

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Abstract

Glass sample of Lead Lithium Borophosphate (50-x) P_2O_5:10Li_2O: 15PbO:25 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 lead lithium borophosphate glasses have been recorded at room temperature. The various interaction parameters like Slater-Condon parameter F_2, Lande' parameter (ξ_{4f}), nephelauexetic ratio (β') and bonding parameter ($b^{1/2}$) have been computed. Judd-Ofelt intensity parameters Ω_λ (λ = 2, 4, 6) and laser parameters have also been calculated.

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

Introduction

Glass materials doped with rare earth ions are widely used mainly for near-infrared solid-state lasers, optical amplifiers, up-conversion systems [1-5]. Glass as a material is comparatively cheap, relatively easy to produce as well as use for synthesis in a wide range of compositions. Glasses with rare earth ions are one of the functional optical materials. Glasses are in particularly suitable for rare earth ions due to higher solubility in host glass matrix [6]. Phosphate glasses have a best thermo-optical performance with considerable chemical durability, high gain as with low energy back transfer and weak up conversion [7-10].

Recently, phosphate glasses have received a great deal of attention due to their potential application in optical data transmission, detection, sensing and laser technology, waveguide [11–14]. When compared with borate and silicate glasses these glasses have distinctive optical properties such as large infrared transmission window, high gain density, low up conversion and wide bandwidth emission spectra [15, 16].

The aim of the present study is to prepare the Tb^{3+} doped lead lithium borophosphate 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.

Experimental Techniques

Preparation of glasses

The following Tb^{3+} doped phosphate glass samples (50-x) P_2O_5:10Li_2O: 15PbO:25 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 P_2O_5, B_2O_3, Li_2O and PbO 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 360^0C 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 %)
LLBP (UD)	$50P_2O_5$:$10Li_2O$: 15PbO:25 B_2O_3
LLBP (TB1)	$49P_2O_5$:$10Li_2O$: 15PbO:25 B_2O_3:1 $Tb_2O_{3.3}$
LLBP (TB1.5)	$48.5P_2O_5$:$10Li_2O$: 15PbO:25 B_2O_3:1.5 $Tb_2O_{3.}$
LLBP (TB 2)	$48P_2O_5$:$10Li_2O$: 15PbO:25 B_2O_3:2 $Tb_2O_{3.}$

LLBP (UD) -Represents undoped Lead Lithium Borophosphate glass specimen.
LLBP (TB) -Represents Tb^{3+} doped Lead Lithium Borophosphate glass specimens.

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 (*ν*) 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 [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.

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 $|4f^N (S, L) J\rangle$ 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, ν 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 (Table 4).

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:

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

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

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

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

Where, the sum is over all terminal manifolds.

The radiative life time is given by

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

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

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

Where, λp 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 [21, 22]. The Nephelauxetic Ratio is given by

$$\beta' = \nu_g / \nu_a \qquad (8)$$

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

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

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.

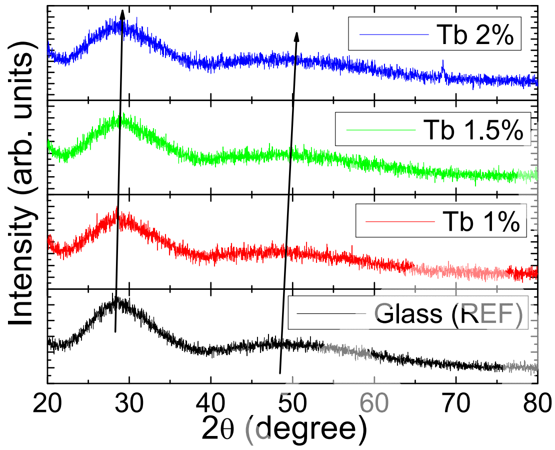

Fig. 1: X-ray diffraction pattern of P_2O_5:PbO: Li_2O: B_2O_3: Tb_2O_3.

Thermal Property

Figure 2 shows the thermal properties of LLBP glass from 300^{0}C to 1000^{0}C. 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 351,450 and 583 respectively. The T_g increase with the contents of Tb_2O_3 increase. We could conclude that thermal properties of the LLBP glass are good for fiber drawing from the analysis of DSC curve.

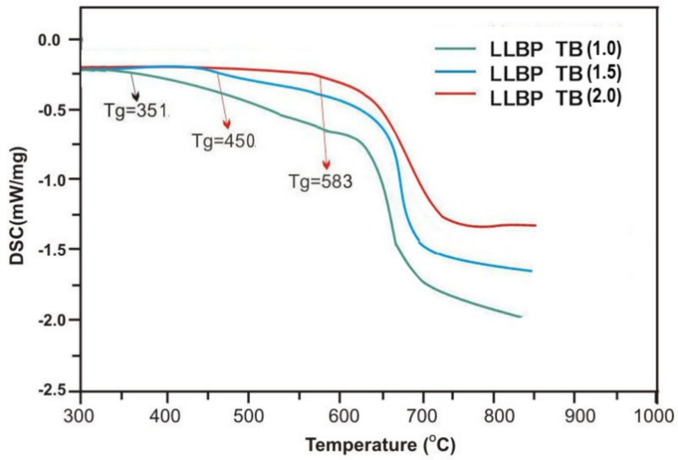

Fig.2: DSC curve of LLBP (TB) glasses.

Absorption Spectrum

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

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

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

Energy level from $^7F_6$	**Glass LLBP (TB01)**		**Glass LLBP (TB1.5)**		**Glass LLBP (TB02)**	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^5D_4$	0.58	0.042	0.56	0.045	0.53	0.50
$^5D_3$,$^5G_6$	0.87	0.33	0.85	0.34	0.82	0.36
$^5L_{10}$	1.64	1.14	1.62	1.15	1.60	1.18
$^5D_2$,$^5G_4$,$^5G_5$	1.86	0.53	1.84	0.54	1.82	0.56
$^5L_9$	2.16	0.99	2.14	1.00	2.12	1.03
r.m.s. deviation		0.8906		0.8648		0.8257

Computed values of F_2, Lande's parameter (ξ_{4f}), Nephlauxetic ratio(β') and bonding parameter($b^{1/2}$) for Tb^{3+} doped LLBP 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 $\Omega_2 > \Omega_6 > \Omega_4$. The spectroscopic quality factor (Ω_4 /Ω_6) related with the rigidity of the glass system has been found to lie between 0.459 and 0.484in the present glasses. The value of Judd-Ofelt intensity parameters are given in Table 4

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

Glass Specimen	**Ω_2(pm^2)**	**Ω_4(pm^2)**	**Ω_6(pm^2)**	**Ω_4 /Ω_6**	**References**
LLBP(TB01)	2.894	1.115	2.430	0.4588	P.W.
LLBP (TB1.5)	3.156	1.208	2.449	0.4933	P.W.
LLBP (TB02)	3.968	1.213	2.508	0.4837	P.W.
WNT (PR)	6.90	3.50	5.20	0.6731	[23]
SZP(DY)	2.15	0.04	0.82	0.0488	[24]

Fluorescence Spectrum

The fluorescence spectrum of Tb^{3+}doped in Lead lithium borophosphate glass is shown in Figure 4. There are four bands observed in the Fluorescence spectrum of Tb^{3+}doped lead lithium borophosphate 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.

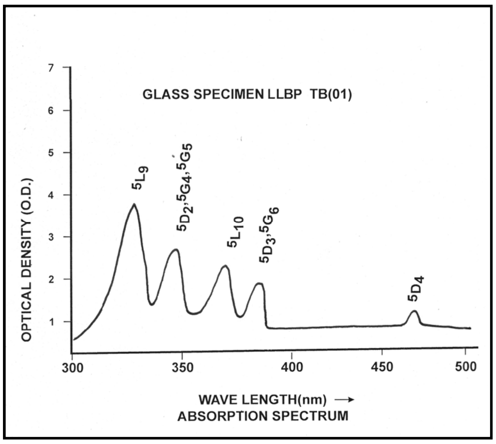

Fig.3: Absorption spectrum of Tb^{3+}doped LLBP (01) glass

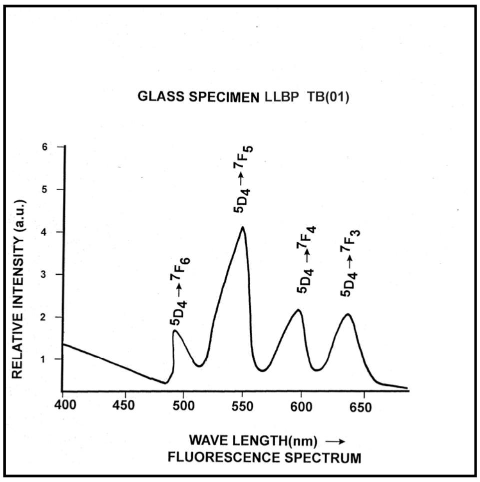

Fig.4: fluorescence spectrum of Tb^{3+}doped LLBP (01) glass

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 LLBP glasses.

Transition		LLBP TB 01				LLBP TB 1.5				LLBP 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	1794.93	0.1177	0.2346		1889.40	0.1153	0.2429		2116.07	0.1080	0.2677	
$^5D_4 \rightarrow {}^7F_5$	550	10079.40	0.6611	1.532	65.59	10908.90	0.6656	1.651	61.02	13377.20	0.6830	2.0163	51.05
$^5D_4 \rightarrow {}^7F_4$	582	1406.58	0.0922	0.4454		1473.19	0.0899	0.4568		1541.58	0.0787	0.4689	
$^5D_4 \rightarrow {}^7F_3$	625	1965.07	0.1289	0.4336		2117.62	0.1292	0.4562		2552.09	0.1303	0.5459	

Conclusion

In the present study, the glass samples of composition (50-x) P_2O_5:10Li_2O: 15PbO:25 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, branching ratio are 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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