Spectral and Thermal Properties of Ho3+ Doped in Lead Lithium Bismuth Silicate Glasses

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Abstract

Glass sample of Lead Lithium Bismuth Silicate (60-x) Bi_2O_3:10PbO:$10Li_2O$:$20SiO_2$: x Ho_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 Ho^{3+} doped lead lithium bismuth silicate glasses have been recorded at room temperature. The various interaction parameters like Slater-Condon parameters F_k (k=2,4,6), Lande' parameters (ξ_{4f}), nephelauexetic ratio (β'),bonding parameters ($b^{1/2}$)and Racah parameters E^k(k=1,2 3) have been computed. Judd-Ofelt intensity parameters and laser parameters have also been calculated.

Keywords: Lead Lithium Bismuth Silicate Glasses, Energy Interaction Parameters, Optical Properties, Judd-Ofelt Analysis.

Introduction

Glasses are good host for rare earth ions, easy to make and at the same time they can be tailored for specific applications [1-4]. The past literature shows that the rare earth ions find more important application in the preparation of the laser materials [5-8].

Review of Literature

The stimulated emission cross-section (σ_p) parameter is the most important parameter. Its value signifies the rateof energy extraction from the laser material and is generally used to predict laser action in different rare earth doped glass specimens. High refractive index of the host material, large line strength and small fluorescence line widths are required to obtain large stimulated emission cross-section favorable for high gain and rapid energy extraction [9, 10]. Recently, many rare earth ions-doped glasses found important in the area of solid state lasers, fiber laser, wave guide laser, laser amplifier in optical communication and optical data storage [11-13].

Aim of the Study

The aim of the present study is to prepare the Ho^{3+} doped Lead lithium bismuth silicate glass with different Ho_2O_3 concentrations. The absorption spectra, fluorescence spectra of $Ho^{3+}$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. To understand the laser efficiency of these materials, the value of spectroscopy quality factor (Ω_4/ Ω_6) has been evaluated.

Experimental Techniques

Preparation of Glasses

The following Ho^{3+} doped bismuth silicate glass samples (60-x) Bi_2O_3:10PbO:$10Li_2O$:$20SiO_2$: x Ho_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, PbO, Li_2O, SiO_2 and Ho_2O_3. They were thoroughly mixed by using an agate pestle mortar. then melted at 1462^0C 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 392^0C 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 %)
LLBS (UD)	60 Bi_2O_3:10PbO:10Li_2O:20SiO_2
LLBS (HO1)	59 Bi_2O_3:10PbO:10Li_2O:20SiO_2: 1 Ho_2O_3
LLBS (HO 1.5)	58.5 Bi_2O_3:10PbO:10Li_2O:20SiO_2: 1.5 Ho_2O_3
LLBS (HO 2)	58 Bi_2O_3:10PbO:10Li_2O:20SiO_2:2 Ho_2O_3

LLBS (UD) -Represents undoped Lead Lithium Bismuth Silicate glass specimens
LLBS (HO) -Represents Ho^{3+} doped Lead Lithium Bismuth Silicate glass specimens

Theory

Oscillator Strength

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

$f_{expt.} = 4.318 \times 10^{-9} \int \varepsilon(v)\, d v$ (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 [15], using the modified relation:

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

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 [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:

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

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

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

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 .

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:

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

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

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

Where, the sum is over all terminal manifolds.
The radiative life time is given by

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

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'> to a final manifold
│$4f^N$ (S, L) J >| is expressed as

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

Where, λ_p the peak fluorescence wavelength of the emission band and $\Delta\lambda_{eff}$ 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 Parameters ($b^{1/2}$), which are computed by using following formulae [18, 19]. The Nephelauxetic Ratio is given by

$$\beta' = \frac{v_g}{v_a} \quad (8)$$

Where, v_a and v_g 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

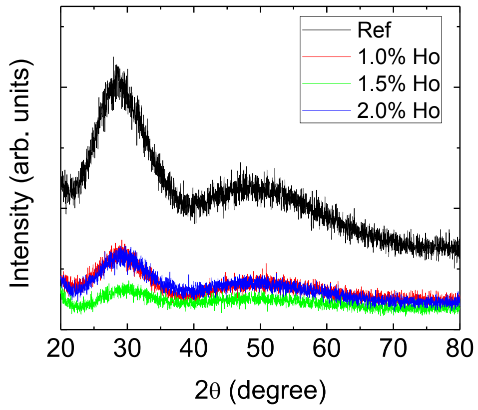
$$b^{1/2} = \left[\frac{1-\beta'}{2}\right]^{1/2} \quad (9)$$

Result and Discussion

XRD Measurement

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

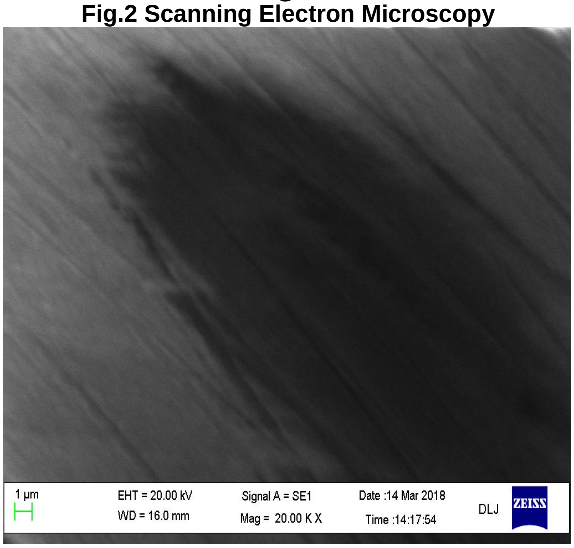
Fig. 1: X-ray Diffraction Pattern of Bi_2O_3: Li_2O: PbO: SiO_2: Ho_2O_3



Scanning Electron Microscopy (SEM)

SEM image explores the smooth surface of the sample. This smooth surface indicates that the amorphous behavior of the glass matrix and also we cannot identified any grain boundaries from the surface morphological image of the host LLBS glass sample as shown in Fig. 2

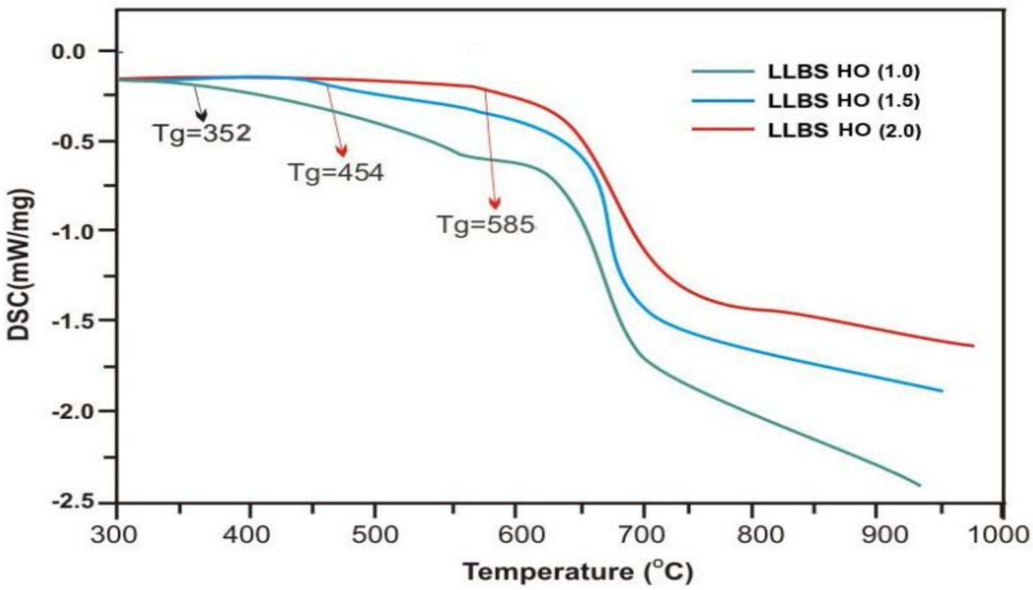
Fig.2 Scanning Electron Microscopy



Thermal Properties

Figure 3 shows the thermal properties of LLBS 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 352^{0}C, 454^{0}C and 585^{0}C respectively. The T_g increase with the contents of Ho_2O_3 increase. We could conclude that thermal properties of the LLBS glass are good for fiber drawing from the analysis of DSC curve.

Fig.3: DSC curve of LLBS (HO) Glasses

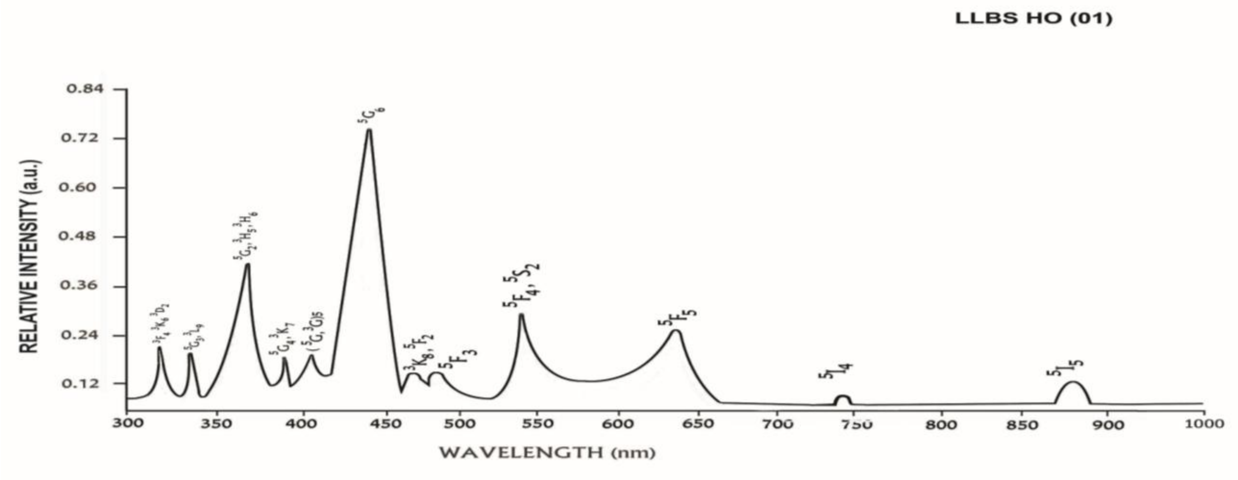


Absorption Spectrum

The absorption spectra of Ho^{3+} doped LLBS (HO 01) glass specimen has been presented in Figure 4 in terms of optical density versus wavelength (nm).

Twelve absorption bands have been observed from the ground state $^5I_8$ to excited states $^5I_5$, $^5I_4$, $^5F_5$, $^5F_4$, $^5F_3$, $^3K_8$, $^5G_6$, $(^5G,^3G)_5$, $^5G_4$, $^5G_2$, $^5G_3$, and $^3F_4$ for Ho^{3+} doped LLBS (HO) glasses.

Figure. 4
Absorption Spectrum of Ho^{3+}doped LLBS Glass



The experimental and calculated oscillator strengths for Ho^{3+} ions in Lead lithium bismuth silicate glasses are given in Table 2

Table2: Measured and calculated oscillator strength ($P_m \times 10^{+6}$) of Ho^{3+}ions in LLBS Glasses

Energy level from $^5I_8$	Glass LLBS (HO01)		Glass LLBS (HO1.5)		Glass LLBS (HO02)	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^5I_5$	0.329	0.242	0.328	0.239	0.325	0.235
$^5I_4$	0.043	0.022	0.042	0.022	0.041	0.022
$^5F_5$	3.50	2.74	3.40	2.71	3.20	2.65
$^5F_4$, $^5S_2$	4.54	4.31	4.52	4.26	4.51	4.18
$^5F_3$	1.57	2.41	1.56	2.39	1.54	2.35
$^3K_8$, $^5F_2$	1.37	1.97	1.36	1.95	1.34	1.92
$^5G_6$	23.66	23.68	23.64	23.67	23.63	23.67
$(^5G, {}^3G)_5$	3.36	1.57	3.34	1.56	3.33	1.52
$^5G_4$, $^3K_7$	0.09	0.60	0.08	0.596	0.06	0.59
$^5G_2$, $^3H_5$	5.24	5.27	5.22	5.26	5.21	5.24
$^5G_3$, $^3L_9$	1.80	1.37	1.70	1.36	1.60	1.35
$^3F_4$, $^3K_6$	1.35	3.94	1.34	3.89	1.32	3.80
r.m.s. deviation		1.0017		0.9867		0.9666

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

Table 3
F_2, ξ_{4f}, β' and $b^{1/2}$ parameters for Holmium Doped Glass Specimen

Glass Specimen	F_2	ξ_{4f}	β'	$b^{1/2}$
Ho^{3+}	427.89	2196.01	0.9718	0.1187

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 0.5610 and 0.5655 in the present glasses.

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

Table 4
Judd-Ofelt Intensity Parameters for Ho^{3+}doped LLBS Glass Specimens

Glass Specimen	Ω_2 (pm^2)	Ω_4 (pm^2)	Ω_6 (pm^2)	Ω_4 /Ω_6	Ref.
LLBS (HO01)	5.109	1.075	1.901	0.5655	P.W.
LLBS (HO1.5)	5.113	1.062	1.881	0.5646	P.W.
LLBS (HO02)	5.127	1.034	1.843	0.5610	P.W.
ZLBB (HO)	4.80	0.945	1.673	0.5649	[20]

Fluorescence Spectrum

The fluorescence spectrum of Ho^{3+} doped in Lead lithium bismuth silicate glass is shown in Figure 5. There are two bands ($^5F_4$, $^5S_2 \rightarrow {}^5I_8$) and ($^5F_5 \rightarrow {}^5I_8$) respectively for glass specimens.

Fig.5: Fluorescence Spectrum of Ho^{3+}doped LLBS HO (01) Glass

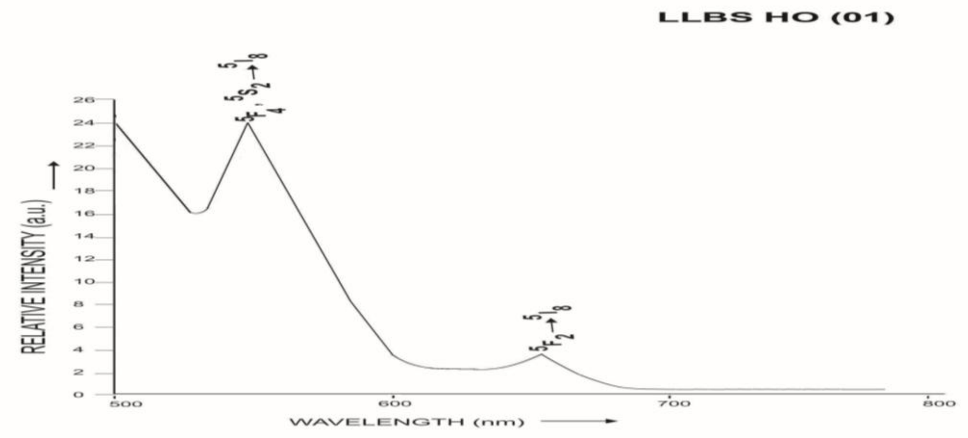


Table 5 Emission Peak Wave Lengths (Λ_p), Radiative Transition Probability (A_{rad}), Branching Ratio (B), Stimulated Emission Cross-Section(Σ_p) And Radiative Life Time(τ_R) for Various Transitions in Ho^{3+} doped LLBS (HO) glasses

Transition		LLBS HO (01)				LLBS HO (1.5)				LLBS (HO 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)
$^5F_4$, $^5S_2 \rightarrow {}^5I_8$	555	5931.03	0.7238	1.126	122.02	5878.60	0.7237	2.130	123.11	5774.03	0.7238	1.055	125.36
$^5F_5 \rightarrow {}^5I_8$	652	2263.80	0.2762	1.072		2244.21	0.2763	1.549		2203.12	0.2762	0.998	

Conclusion

In the present study, the glass samples of composition (60-x) Bi_2O_3:10PbO:10Li_2O:20SiO_2: x Ho_2O_3. (where x=1,1.5, 2) have been prepared by melt-quenching method. The spectroscopic quality factor (Ω_4 /Ω_6) related with the rigidity of the glass system has been found to lie between0.5610 and 0.5655 in the present glasses.

The radiative transition probability, branching ratio are highest for ($^5F_4$,$^5S_2 \rightarrow {}^5I_8$) transition and hence it is useful for laser action. The stimulated emission cross section (σ_p) has highest value for the transition ($^5F_4$, $^5S_2 \rightarrow {}^5I_8$) in all the glass specimens doped with Ho^{3+}ion. This shows that ($^5F_4$, $^5S_2 \rightarrow {}^5I_8$) transition is most probable transition.

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