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SPECTROSCOPIC PROPERTIES OF SM^{3+} DOPED IN YTTERBIUM LEAD LITHIUM BISMUTH SILICATE GLASSES

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ABSTRACT

Glass sample of Ytterbium Lead Lithium Bismuth Silicate (50-x) Bi_2O_3:10PbO:10Li_2O: 10Yb_2O_3: 20SiO_2: x Sm_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 Sm^{3+} doped Ytterbium 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: *Ytterbium lead lithium bismuth silicate glasses, Energy interaction parameters, Optical properties, Judd-Ofelt analysis.*

1. INTRODUCTION

Glasses are important optical materials usually made to be transparent in the visible spectrum [1-4]. In general, the optical and spectroscopic properties of rare earth ions are strongly dependent on host materials. Silicate glasses are more suitable due to its high refractive index and low phonon energy. Rare-earth doped glasses have been paid much attention because of their high potential use for optical application such sensors as well as LED devices [5-7]. Recently, many rare earth ions-doped glasses found important in the area of solid state lasers, fiber laser and wave guide laser [8-10].

The aim of the present study is to prepare the Sm^{3+} doped ytterbium lead lithium bismuth silicate glass with different Sm_2O_3 concentrations. The absorption spectra, fluorescence spectra of $Sm^{3+}$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.

2. Experimental Techniques

Preparation of glasses

The following Sm^{3+} doped bismuth silicate glass samples (50-x) Bi_2O_3:10PbO:10Li_2O: 10Yb_2O_3:20SiO_2: x Sm_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, PbO,Yb_2O_3, SiO_2 and Sm_2O_3. They were thoroughly mixed by using an agate pestle mortar. then melted at 1180^{0}C 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 380^{0}C 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 %)
YLLBS (UD)	50 Bi_2O_3:10PbO:10Li_2O: 10Yb_2O_3: 20SiO_2:
YLLBS (SM1)	49 Bi_2O_3:10PbO:10Li_2O: 10Yb_2O_3: 20SiO_2: 1 Sm_2O_3.
YLLBS (SM 1.5)	48.5Bi_2O_3:10PbO:10Li_2O: 10Yb_2O_3: 20SiO_2: 1.5 Sm_2O_3.
YLLBS (SM 2)	48 Bi_2O_3:10PbO:10Li_2O: 10Yb_2O_3: 20SiO_2: 2 Sm_2O_3.

YLLBS (UD) -Represents undoped Ytterbium Lead Lithium Bismuth Silicate glass specimens.
YLLBS (SM) -Represents Sm^{3+} doped Ytterbium Lead Lithium Bismuth Silicate glass specimens.

3. THEORY

3.1 Oscillator Strength

The intensity of spectral lines is expressed in terms of oscillator strengths using the relation [11].

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

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 [12], 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, 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 [13] and Ofelt [14] 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

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

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 ($\lambda = 2, 4, 6$) are known as Judd-Ofelt intensity parameters.

3.3 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:

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

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

The fluorescence branching ratio for the transitions originating from a specific initial manifold |4fN (S', L') J'> to a final many fold $|4f^N$ (S, L) J > is given by

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

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

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

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

3.4 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 [15, 16]. The Nephelauxetic Ratio is given by

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

where, ν_a and ν_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

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

4. RESULT AND DISCUSSION

4.1 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.

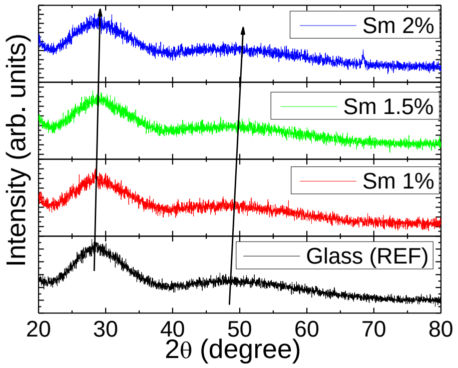

Fig. 1: X-ray diffraction pattern of Bi_2O_3: PbO: Li_2O: Yb_2O_3: SiO_2: Sm_2O_3.

4.2 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 YLLBS glass sample as shown in Fig. 2

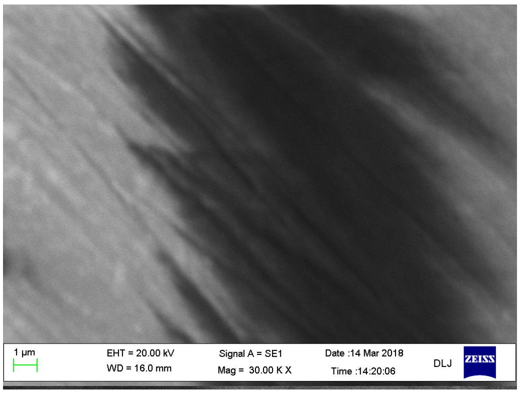

Fig.2 Scanning Electron Microscopy

4.3 Thermal Properties

Figure 3 shows the thermal properties of YLLBS 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 352^0C, 451^0C and 580^0C respectively. The T_g increase with the contents of Sm_2O_3 increase. We could conclude that thermal properties of the YLLBS glass are good for fiber drawing from the analysis of DSC curve.

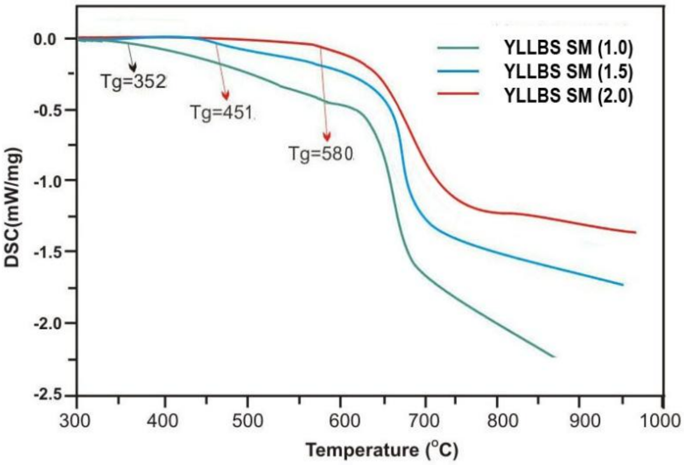

Fig.3: DSC curve of YLLBS(SM) glasses.

4.3 Absorption Spectrum

The absorption spectra of Sm^{3+} doped YLLBS (SM 01) glass specimen has been presented in Figure 4 in terms of optical density versus wavelength (nm). Ten absorption bands have been observed from the ground state $^6H_{5/2}$ to excited states $^6F_{1/2}$, $^6F_{7/2}$, $^6F_{9/2}$, $^4G_{7/2}$,$^4I_{9/2}$, $^4M_{7/2}$, $(^6P,^4P)_{5/2}$, $^4F_{7/2}$, $^4D_{1/2}$, and $(^4D,^6P)_{5/2}$ for Sm^{3+} doped YLLBS glasses.

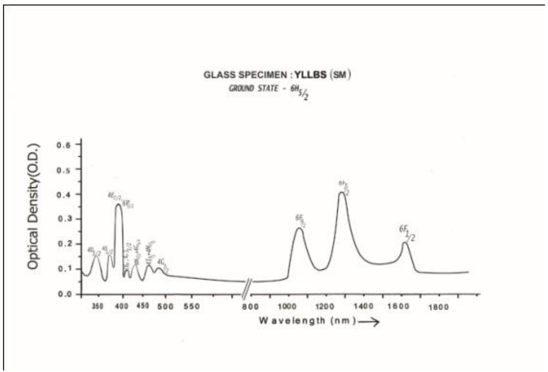

Fig.4: Absorption spectrum of Sm^{3+}doped YLLBS (01) glass

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

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

Energy level from $^6H_{5/2}$	**Glass** YLLBS **(SM01)**		**Glass** YLLBS **(SM1.5)**		**Glass** YLLBS **(SM02)**	
	P_{exp}.	P_{cal}.	P_{exp}.	P_{cal}.	P_{exp}.	P_{cal}.
$^6F_{1/2}$	1.57	1.63	1.56	1.62	1.54	1.60
$^6F_{7/2}$	5.43	5.50	5.42	5.49	5.41	5.48
$^6F_{9/2}$	3.78	3.83	3.75	3.82	3.74	3.82
$^4G_{7/2}$	0.16	0.18	0.14	0.12	0.13	0.12
$^4I_{9/2}$,$^4M_{15/2}$,$^4I_{11/2}$	1.13	1.88	1.12	1.87	1.09	1.87
$^4M_{17/2}$,$^4G_{9/2}$,$^4I_{15/2}$	0.27	0.25	0.26	0.24	0.24	0.24
$(^6P,^4P)_{5/2}$,$^4L_{13/2}$	1.29	1.30	1.27	1.31	1.26	1.30
$^4F_{7/2}$,$^6P_{3/2}$,$^4K_{11/2}$	5.53	5.60	5.52	5.62	5.50	5.62
$^4D_{1/2}$,$^6P_{7/2}$,$^4L_{17/2}$	2.40	2.42	2.38	2.42	2.37	2.42
$^4D_{3/2}$, $(^4D,^6P)_{5/2}$	2.43	3.45	2.42	3.46	2.39	3.45
r.m.s. deviation	±0.403		±0.408		±0.420	

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

Table 3. F_2, ξ_{4f}, β' and $b^{1/2}$ parameters for Samarium doped glass specimen.

Glass Specimen	F_2	ξ_{4f}	β'	$b^{1/2}$
Sm^{3+}	358.82	1258.16	0.9337	0.1821

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 1.0903 and 1.102 in the present glasses.

The value of Judd-Ofelt intensity parameters are given in **Table4**

Table4: Judd-Ofelt intensity parameters for Sm^{3+} doped YLLBS glass specimens.

Glass Specimen	**$\Omega_2(pm^2)$**	**$\Omega_4(pm^2)$**	**$\Omega_6(pm^2)$**	**Ω_4/Ω_6**	**Ref.**
YLLBS (SM01)	4.216	3.874	3.545	1.093	P.W.
YLLBS (SM1.5)	4.195	3.880	3.523	1.101	P.W.
YLLBS (SM02)	4.150	3.875	3.517	1.102	P.W.
LBGS(SM)	9.93	9.84	7.51	1.30	[17]

4.4. Fluorescence spectrum

The fluorescence spectrum of Sm^{3+}doped in ytterbium lead lithium bismuth silicate glass is shown in Figure 5. There are four bands observed in the Fluorescence spectrum of Sm^{3+}doped ytterbium lead lithium bismuth silicate glass. The wavelengths of these bands along with their assignments are given in Table 5. Fig. (4).Shows the fluorescence spectrum with four peaks ($^4G_{5/2}\rightarrow{}^6H_{5/2}$), ($^4G_{5/2}\rightarrow{}^6H_{7/2}$), ($^4G_{5/2}\rightarrow{}^6H_{9/2}$) and ($^4G_{5/2}\rightarrow{}^6H_{11/2}$), respectively for glass specimens.

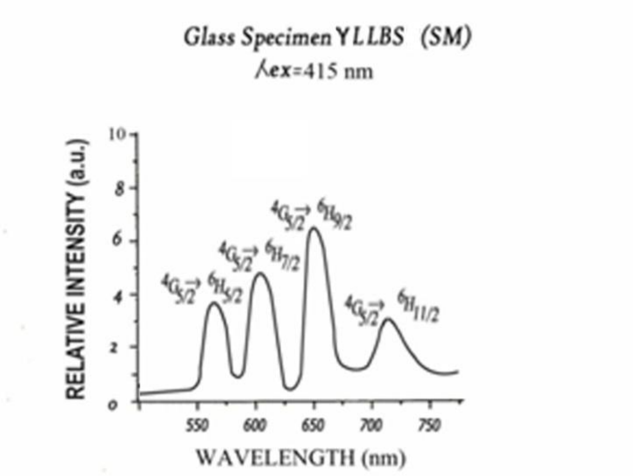

Fig.5: fluorescence spectrum of Sm^{3+}doped YLLBS (01) glass

Table 5. 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 Sm^{3+} doped YLLBS glasses

Transition		YLLBS SM 01				YLLBS SM 1.5				YLLBS SM 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 (10^{-20} cm^2)	$\tau_R(\mu s)$	$A_{rad}(s^{-1})$	β	σ_p (10^{-20} cm^2)	$\tau_R(\mu s)$
$^4G_{5/2}\rightarrow{}^6H_{5/2}$	563	13.379	0.0413	0.0040	3085.74	13.413	0.0414	0.0044	3083.80	13.373	0.0413	0.0047	3091.29
$^4G_{5/2}\rightarrow{}^6H_{7/2}$	600	141.608	0.4370	0.0463		141.717	0.4370	0.0494		141.701	0.4380	0.0533	
$^4G_{5/2}\rightarrow{}^6H_{9/2}$	647	134.499	0.4150	0.0448		134.478	0.4147	0.0473		133.746	0.4134	0.0495	
$^4G_{5/2}\rightarrow{}^6H_{11/2}$	705	34.586	0.1067	0.0135		34.668	0.1069	0.0137		34.669	0.1072	0.0143	

5. CONCLUSION

In the present study, the glass samples of composition (50-x) Bi_2O_3:10PbO:10Li_2O: 10Yb_2O_3: 20SiO_2: x Sm_2O_3 (where x=1, 1.5, 2mol %) have been prepared by melt-quenching method. The Judd-Ofelt theory has been applied to calculate the oscillator strength and intensity parameters Ω_λ (λ=2, 4, 6).The Ω_2 parameter shows the covalent nature of the prepared glass. The stimulated emission cross section (σ_p) has highest value for the transition ($^4G_{5/2}\rightarrow{}^6H_{7/2}$) in all the glass specimens doped with Sm^{3+} ion. This shows that ($^4G_{5/2}\rightarrow{}^6H_{7/2}$) transition is useful for laser action.

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