International Journal of Engineering Science Invention (IJESI)
ISSN (Online): 2319-6734, ISSN (Print): 2319-6726
www.ijesi.org ||Volume 11 Issue 2 Series I || February 2022 || PP 44-49

Spectral and Up conversion Properties of Dy^{3+} ions doped Zinc Lithium Potessiumniobate Borosilicate Glasses

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Abstract
Glass of the system: (35-x)SiO_2:10ZnO:10Li_2O:10K_2O:10Nb_2O_5:25B_2O_3: xDy_2O_3. (where x=1, 1.5,2 mol %) have been prepared by melt-quenching method. The amorphous nature of the glasses was confirmed by X-ray diffraction studies. Optical absorption, excitation and emission spectra were recorded at room temperature for all glass samples. Judd-Ofelt intensity parameters Ω_λ (λ=2, 4 and 6) are evaluated from the intensities of various absorption bands of optical absorption spectra. Using these intensity parameters various radiative properties like spontaneous emission probability, branching ratio, radiative life time and stimulated emission cross–section of various emission lines have been evaluated

Keywords: *ZLPNBS Glasses, Optical Properties, Judd-Ofelt Theory, Up conversion Properties.*

Date of Submission: 05-02-2022 Date of Acceptance: 18-02-2022

I. INTRODUCTION

Rare earth glasses have attracted much attention, because they have large practical and potential applications in many fields, such as glass lasers, optical fiber amplifiers, sensor energy storage and communication[1-5].Transparent glass-ceramic as host materials for active optical ions have attracted great interest due their potential application in optical devices such as optical amplifiers, lasers, frequency-conversion materials[6-8].Silicate glasses possess higher thermal damage threshold than other glasses, because the main componenet is SiO_2.Recently silicate based glasses have a wide range of potential applications in optical data transmission, sensing and laser technologies [9-12]. B_2O_3 is excellent material for combination with SiO_2 as it improves the glass quality in terms of transparency and hardness [13].Up conversion is a non-linear optical phenomenon which involves the sequential absorption of two or more low energy (NIR) photon to emit a high energy (visible) photon. In recent decades, the upconversion materials have been extensively investigated due to their potential applications in many fields, such as sensor, solar cell and color display. The up-conversion of silicate glasses is also compressed because of their relatively large phonon energy [14-18].

The present work reports on the preparation and characterization of rare earth doped heavy metal oxide (HMO) glass systems for lasing materials. I have studied on the absorption, excitation and emission properties of Dy^{3+} doped zinc lithium potassiumniobate borosilicate glasses. The intensities of the transitions for the rare earth ions have been estimated successfully using the Judd-Ofelt theory, The laser parameters such as radiative probabilities(A),branching ratio (β), radiative life time(τ_R) and stimulated emission cross section(σ_p) are evaluated using J.O.intensity parameters(Ω_λ, λ=2,4 and 6).

II. EXPERIMENTAL TECHNIQUES

Preparation of glasses

The following Dy^{3+}doped silicate glass samples (35-x)SiO_2:10ZnO:10Li_2O:10K_2O:10Nb_2O_5:25B_2O_3: xDy_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 SiO_2, ZnO, Li_2O, K_2O,Nb_2O_5, B_2O_3 and Dy_2O_3. They were thoroughly mixed by using an agate pestle mortar. then melted at 1060^{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 350^{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 %)
ZLPNBS (UD)	$35SiO_2:10ZnO:10Li_2O:10K_2O:10Nb_2O_5:25B_2O_3$.
ZLPNBS (DY1)	$34SiO_2:10ZnO:10Li_2O:10K_2O:10Nb_2O_5:25B_2O_3:1\ Dy_2O_3$.
ZLPNBS (DY1.5)	$33.5SiO_2:10ZnO:10Li_2O:10K_2O:10Nb_2O_5:25B_2O_3:1.5\ Dy_2O_3$.
ZLPNBS (DY2)	$33SiO_2:10ZnO:10Li_2O:10K_2O:10Nb_2O_5:25B_2O_3:\ 2\ Dy_2O_3$.

ZLPNBS (UD) -Represents undoped Zinc Lithium Potassiumniobate Borosilicate glass specimens.
ZLPNBS (DY)-Represents Dy^{3+} doped Zinc Lithium Potassiumniobate Borosilicate glass specimens.

III. THEORY

3.1 Oscillator Strength

The intensity of spectral lines are expressed in terms of oscillator strengths using the relation [19].

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

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 [20], 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 [21] and Ofelt [22] 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

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

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=2,4and 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:

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

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

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

$$\beta [(S', L') J'; (S, L) J] = \sum_{SLJ} \frac{A[(S' L)]}{A[(S' L') J' (\bar{S} L)]} \quad (6)$$

where, the sum is over all terminal manifolds.

The radiative life time is given by

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

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

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

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 [23,24]. The Nephelauxetic Ratio is given by

$$\beta' = \frac{\nu_g}{\nu_a} \quad (9)$$

where, ν_a and ν_g refer to the energies of the corresponding transition in the glass and free ion, respectively. The value of bonding parameter ($b^{1/2}$) is given by

$$b^{1/2} = \left[\frac{1-\beta'}{2}\right]^{1/2} \quad (10)$$

IV. RESULT AND DISCUSSION

4.1 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.

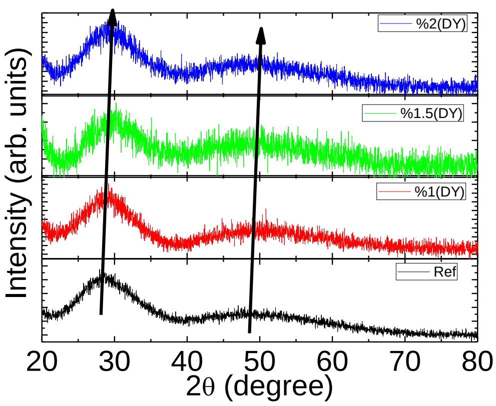

Fig. 1 X-ray diffraction pattern of SiO_2:ZnO:Li_2O:K_2O:Nb_2O_5:B_2O_3:Dy_2O_3

4.2 Absorption Spectrum

The absorption spectrum of ZLPNBS DY (01) glass specimen has been presented in Figure 2 in terms of optical density versus wavelength. Thirteen absorption bands have been observed from the ground state $^6H_{15/2}$ to excited states $^6H_{13/2}$, $^6H_{11/2}$, $^6H_{9/2}$+$^6F_{11/2}$, $^6H_{7/2}$+$^6F_{9/2}$, $^6F_{7/2}$+$^6H_{5/2}$, $^6F_{5/2}$, $^6F_{3/2}$, $^6F_{9/2}$, $^4I_{15/2}$, $^4G_{11/2}$, $^6F_{7/2}$+$^4I_{13/2}$, $^6M_{19/2}$+4(P,D)$_{3/2}$ and $^4G_{9/2}$+$^6P_{3/2}$ for ZLPNBS DY(01)glass.

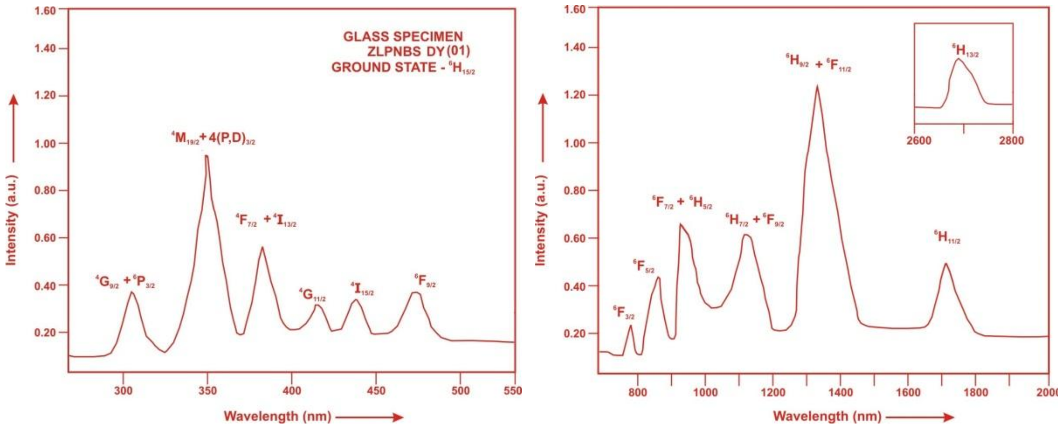

Fig. (2) Absorption spectrum of ZLPNBS DY (01) glass.

4.3 Excitation Spectrum

The Excitation spectrum of ZLPNBS DY (01) glass specimen has been presented in Figure 3 in terms of optical density versus wavelength. The excitation spectrum was recorded in the spectral region 300–500 nm fluorescence at 575nm having different excitation band centered at 353, 367, 390, 428, 454 and 474 nm are attributed to the $^6P_{3/2}$, $^6P_{7/2}$, $^6P_{5/2}$, $^4K_{17/2}$, $^4G_{11/2}$, $^4I_{15/2}$ and $^4F_{9/2}$ transitions, respectively. The highest absorption level is $^6P_{7/2}$ and is at 353nm.So this is to be chosen for excitation wavelength.

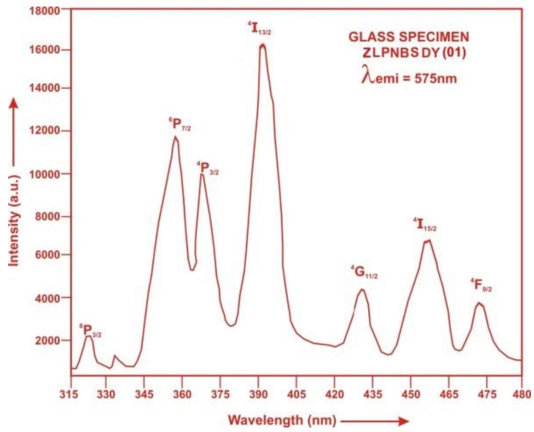

Fig. (3) Excitation spectrum of ZLPNBS DY (01) glass.

The experimental and calculated oscillator strength for Dy^{3+} ions in ZLPNBS glasses are given in **Table 2.**

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

Energy level from $^6H_{15/2}$	**Glass ZLPNBS (DY01)**		**Glass ZLPNBS (DY1.5)**		**Glass ZLPNBS (DY02)**	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^6H_{13/2}$	2.02	2.37	2.00	2.35	1.96	2.34
$^6H_{11/2}$	1.36	1.95	1.33	1.93	1.30	1.91
$^6H_{9/2}+^6F_{11/2}$	10.21	10.10	10.17	10.06	10.14	10.03
$^6H_{7/2}+^6F_{9/2}$	5.52	5.20	5.49	5.18	5.45	5.14
$^6F_{7/2}+^6H_{5/2}$	4.68	3.66	4.65	3.62	4.62	3.58
$^6F_{5/2}$	1.27	1.63	1.25	1.61	1.22	1.58
$^6F_{3/2}$	0.25	0.31	0.23	0.30	0.20	0.30
$^6F_{9/2}$	0.33	0.28	0.30	0.27	0.27	0.27
$^4I_{15/2}$	0.30	0.67	0.28	0.66	0.24	0.65
$^4G_{11/2}$	0.24	0.17	0.22	0.17	0.19	0.17
$^6F_{7/2}+^4I_{13/2}$	3.42	3.61	3.39	3.59	3.36	3.55
$^6M_{19/2}$+4(P,D)3/2	7.92	10.04	7.89	10.03	7.85	10.01
$^4G_{9/2}+^6P_{3/2}$	1.60	2.03	1.58	2.01	1.54	1.99
r.m.s. deviation	0.7136		0.7204		0.7290	

In the Zinc Lithium Potassiumniobate Borosilicate glasses (ZLPNBS) Ω_2, Ω_4 and Ω_6 parameters decrease with the increase of x from 1 to 2 mol%. The order of magnitude of Judd-Ofelt intensity parameters is $\Omega_2 > \Omega_4 > \Omega_6$ for

all the glass specimens. The high values obtained for Ω_2 in all glasses indicate that the Dy^{3+} ion is subjected to higher covalency with low symmetry. The spectroscopic quality factor (Ω_4 /Ω_6) related with the rigidity of the glass system has been found to lie between 1.259 and 1.308 in the present glasses.
The values of Judd-Ofelt intensity parameters are given in **Table 3.**

Table 3: Judd-Ofelt intensity parameters for Dy^{3+} doped ZLPNBS glass specimens.

Glass Specimen	$\Omega_2(pm^2)$	$\Omega_4(pm^2)$	$\Omega_6(pm^2)$	Ω_4 /Ω_6	Ref.
ZLPNBS (DY01)	2.553	1.568	1.245	1.259	P.W.
ZLPNBS (DY1.5)	2.536	1.573	1.229	1.280	P.W.
ZLPNBS (DY02)	2.524	1.577	1.206	1.308	P.W.
BariumFluroborate(DY)	2.90	1.09	0.98	1.112	[25]
Ge-Ga-Sb-S(DY)	11.61	2.79	1.11	2.514	[26]

4.4. Fluorescence Spectrum

The fluorescence spectrum of Dy^{3+}doped in zinc lithium potassiumniobate borosilicate glass is shown in Figure 4. There are four broad bands observed in the Fluorescence spectrum of Dy^{3+}doped zinc lithium potassiumniobate borosilicate glass. The wavelengths of these bands along with their assignments are given in Table 4. The peak with maximum emission intensity appears at 485nm,575 nm ,665 nm and 752nm and corresponds to the($^4F_{9/2}\rightarrow{}^6H_{15/2}$), ($^4F_{9/2}\rightarrow{}^6H_{13/2}$), ($^4F_{9/2}\rightarrow{}^6H_{11/2}$) and ($^4F_{9/2}\rightarrow{}^6H_{9/2}$) transition.

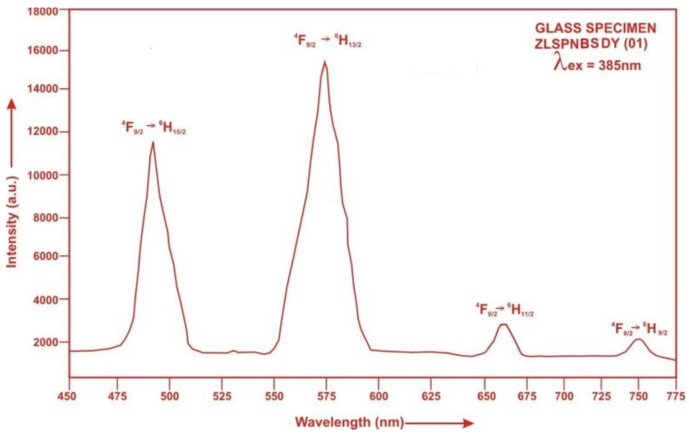

Fig. (4). Fluorescence spectrum of ZLPNBS DY (01) glass.

4.5 Up conversion Mechanism

The up-conversion mechanism is given in Fig. 5

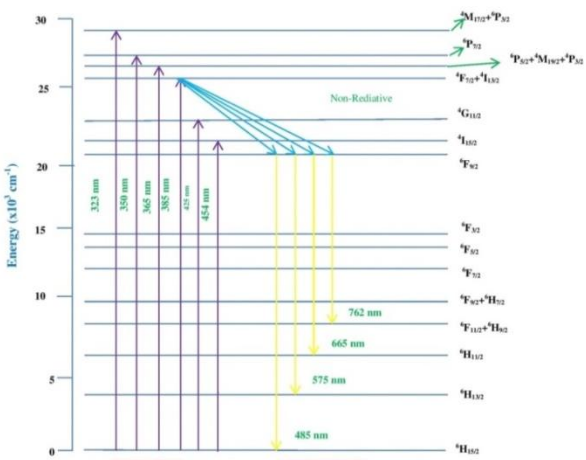

Fig. 5. Energy level diagram of Dy^{3+} ion and up conversion mechanism of Dy^{3+} doped glass ceramic.

Table4: 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 Dy^{3+} doped ZLPNBS glasses.

Transition		ZLPNBS DY 01				ZLPNBS DY 1.5				ZLPNBS DY 02			
	λ_{max} (nm)	$A_{rad}(s^{-1})$	β	σ_p (10^{-20} cm^2)	τ_R(µs)	$A_{rad}(s^{-1})$	β	σ_p (10^{-20} cm^2)	τ_R (µs)	$A_{rad}(s^{-1})$	β	σ_p (10^{-20} cm^2)	τ_R (10^{-20} cm^2)
$^4F_{9/2} \rightarrow {}^6H_{15/2}$	485	90.50	0.1963	0.165	2168.81	89.64	0.1957	0.161	2182.92	88.51	0.1945	0.155	2197.94
$^4F_{9/2} \rightarrow {}^6H_{13/2}$	575	311.52	0.6756	1.205		309.64	0.6759	1.168		307.87	0.6767	1.140	
$^4F_{9/2} \rightarrow {}^6H_{11/2}$	665	32.96	0.0715	0.146		32.80	0.0716	0.144		32.67	0.0718	0.140	
$^4F_{9/2} \rightarrow {}^6H_{9/2}$	752	26.11	0.0566	0.138		26.01	0.0568	0.137		25.92	0.0570	0.134	

V. CONCLUSION

In the present study, the glass samples of composition (35-x)SiO2:10ZnO:10Li2O:10K2O:10Nb2O5:25B2O3: xDy2O3 (where x =1, 1.5and 2mol %) have been prepared by melt-quenching method. The value of stimulated emission cross-section (σp) is found to be maximum for the transition (4F9/2→6H13/2) for glass ZLPNBS (DY01), suggesting that glass ZLPNBS (DY 01) is better compared to the other two glass systems ZLPNBS (DY1.5) and ZLPNBS (DY02).Such optical glasses could be suggested as potential materials for their use in progress of optical lasers and optoelectronic devices.

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