

Research Article

Spectral Studies of Dy³⁺ Doped Heavy Metal Oxide Glasses

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Abstract

 Dy^{3+} : PbO-Bi₂O₃-WO₃-B₂O₃ glass systems have been developed using Melt quenching technique. Spectroscopic and Physical properties of these glass systems have been investigated. The nephalauxetic effects for all the glass systems have been computed. The physical properties such as density (d), molar volume (V), polaron radius (r_p), refractive index (n), inter ionic distance (r_i) have been evaluated. The Judd-Ofelt theory has been applied to the analysis of absorption spectra. The environment sensitive Ω_2 parameter exhibits higher among the other Judd – Ofelt parameters indicate the asymmetry around the rare earth ions in all the glass systems. The radiative lifetimes (τ_R)for certain lasing transitions have been computed. Branching ratios (β_r), absorption (σ_a) and emission cross sections (σ_e) for certain lasing transitions have been reported. The visible luminescence spectra exhibit two intense bands around 480nm, 560nm due to ${}^4F_{9/2}$ - $\rightarrow {}^6H_{15/2}$ (Blue) and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ (Yellow) transition of Dy³⁺. Yellow to blue luminescence ratio (Y/B) for all the glass systems indicate greater than unity.

Keywords: Dysprosium, HMO glasses, Optical materials, photoluminescence.

1. Introduction

Mid infrared laser systems gain considerable importance due to their applications in the areas like military, remote sensing, atmosphere pollution monitors and medicine (S.Tokita et al, 2010), (N. Djeu et al, 1997), (S.D. Jackson et al, 2004), (C. Carbonnier et al, 1998), (D.Lezal et al, 2001). Dy^{3+} doped glass systems are prominent among different crystalline and amorphous media for emission of visible light (R.Praveena et al, 2008), (K. K. Mahato et al, 2005). The emission spectrum of transitions from the excited ${}^{4}F_{9/2}$ state of Dy^{3+} exhibits several lines in the blue, green and red bands. The white light generations in dysprosium based phosphors (A.L. Heyes et al, 2009), (S.A.Allison et al, 1997) are of the good research interest. The lasing transition ${}^{6}H_{13/2} \rightarrow {}^{6}H_{15/2}$ of Dy³⁺ reported in literature (Schweizer et al, 1996), (J.Heo et al, 1997) for 2.8µm laser emission in glass and crystal media is regarded as an important transition for mid-IR lasers. The low phonon energy 250-450cm⁻¹ result in low nonradioactive decay rates among rare earth energy levels and high refractive indices (>2.1) yield large stimulated emission cross sections and high emission efficiencies (B.R.Judd et al, 1962), (K. Wei et al, 1994). Lanthanide doped HMO glasses are good lasing candidates because of their low phonon energy. Lead bismuthate glass systems exhibit high refractive indices, high optical basicity, large polarizability and non-linear optical susceptibilities (S.P.

Singh et al, 2010) which allow them to be potential candidates for application in the areas such as ceramic substrates for optical and electronic devices, thermal and mechanical sensors and reflecting windows. We have made an attempt in our earlier paper (P S R Naik et al, 2012) to elucidate the spectral properties of Eu^{3+} : Lead bismuthate glass systems for good lasing systems. In the present paper we have made an attempt to develop and characterize the Dy³⁺: Lead bismuthate glass systems for their lasing potentialities. The lasing properties of these glass systems such as radiative lifetimes (τ_R), branching ratios (β_r), and absorption (σ_a) and emission cross sections (σ_a) are evaluated. Yellow to blue luminescence ratio (Y/B) were analyzed for all these glass systems. Lifetime of ${}^{4}F_{9/2}$ level of Dy^{3+} transition has been monitored at different concentration of Dy³⁺ ion.

2. Experimental

The following five glass samples of Dy^{3+} doped glass samples in the following molar concentrations were prepared using conventional melt-quenching technique. These glass samples are labeled as

 $\begin{array}{l} LBWBD1: 50PbO + 10Bi_2O_3 + 10WO_3 + 29 \ B_2O_3 + 1Dy_2O_3 \\ LBWBD2: 45PbO + 15Bi_2O_3 + 10 \ WO_3 + 29B_2O_3 + 1Dy_2O_3 \\ LBWBD3: 40PbO + 20Bi_2O_3 + 10WO_3 + 29B_2O_3 + 1Dy_2O_3 \\ LBWBD4: \ 35PbO + 25Bi_2O_3 + 10WO_3 + 29B_2O_3 + Dy_2O_3 \\ LBWBD5: 30PbO + 30Bi_2O_3 + 10WO_3 + 29B_2O_3 + 1Dy_2O_3 \end{array}$

The glass samples were prepared using high purity PbO, Bi_2O_3 , WO_3 , B_2O_3 (H₃BO₃) and Dy_2O_3 powders. A batch of 10 g of the above chemicals were properly

Physical property	LBWBD1	LBWBD2	LBWBD3	LBWBD4	LBWBD5
Average Molecular Weight	203.6	215.8	227.9	240.1	248.5
Density (g/cm ³)	7.44	7.48	7.457	7.579	7.624
Refractive Index 'n'	2.185	2.150	2.115	2.080	2.045
Concentration 'N'(10 ²² ions/cm ³)	2.20	2.08	1.97	1.89	1.848
Polaron radius r_p , (A ⁰)	6.671	6.794	6.92	7.01	7.07
Inter ionic distance r_i (A ⁰)	1.656	1.685	1.717	1.739	1.755
Field strength F $(10^{16} \text{ cm}^{-2})$	6.74	6.49	6.25	6.10	5.99
Molar refractivity ' R_M ' (cm ⁻³)	15.25	15.43	16.40	15.98	16.78
Electronic polarizability (10 ⁻²⁴ cm ⁻³)	6.24	6.25	6.47	6.59	6.74
Molar volume 'V _m '	27.37	28.85	30.56	31.68	32.61
Optical Dielectric Constant (ɛ)	3.77	3.62	3.47	3.32	3.18

Table 1: Physical properties of Dy3+ ions in LBWBD1-5 glasses

Table 2: Experimental energies (cm⁻¹) and bondingparameters (δ) of Dy³⁺: LBWBD 1-5 glasses

Level	LBWBD1	LBWBD2	LBWBD3	LBWBD4	LBWBD5
⁶ H _{11/2}	5931	5952	5952	5972	5952
${}^{6}F_{11/2}$	7857	7836	7837	7857	7857
⁶ F _{9/2}	9186	9146	9165	9165	9165
⁶ F _{7/2}	11149	11110	11110	11130	11130
⁶ F _{5/2}	12479	12460	12479	12479	12479
${}^{6}F_{3/2}$	13313	13293	13313	13332	13392
β ⁻	1.012	1.009	1.010	1.012	1.012
δ	-0.012	-0.009	-0.001	-0.011	-0.012

weighed in an electronic balance, mixed homogeneously and well grinded in an agate mortar for smooth powder. The powder is transferred in to a silica crucible and placed in an electric furnace for heating. Initially the samples were heated at 400 °C for 30 minutes and then heated for melting at about 1000 °C for 1 hour. The melt was poured on a preheated steel plate, which keeps the rare earth ions distribution as homogeneous as in the melt. The glasses thus obtained were annealed at approximately 400°C for several hours to remove thermal strains and then allowed to cool to room temperature. The annealed glass samples were fabricated and polished to the thickness of 0.5cm to facilitate subsequent test measurements. The samples had a typical thickness of approximately 0.5cm. The densities of the glasses were measured by Archimedes principle. The X-ray diffraction spectra were recorded for LBWBD glass on a Shimadzu-XD 3A diffractometer. The UV-Vis-NIR absorption spectra of these glasses were measured on a JASCO V-570 UV/VIS spectrophotometer at room temperature and the photoluminescence studies were carried out on SPEX FLUOROLOG-3 (MODEL-II) visible fluorescence spectrophotometer at room temperature.

3. Results and discussion

3.1 physical properties

Physical properties like refractive index (n), density (d), optical dielectric constant, molar refractivity (R_M), interionic distance (r_i), polaron radius (r_p), average molecular weight, ion concentration (N), molecular electron polarizability (α),and field strength (F) required for computation of radial properties of the glasses are evaluated following the expressions available in the literature (Reddy RR, et al, 2003). These values are presented in Table 1.

3.2 Absorption Spectra

The absorption spectra of all the five glasses namely LBWBD 1-5 were recorded at room temperature in the wave length region of 400-2000nm and are collected in Fig 1. The absorption levels observed are assigned to ${}^{6}\text{H}_{11/2}$, ${}^{6}\text{F}_{11/2}$, ${}^{6}\text{F}_{9/2}$, ${}^{6}\text{F}_{7/2}$ and ${}^{6}\text{F}_{5/2}$ levels following (Carnal et al, 1997). The computed (SurendraBabu S et al, 2009) bonding parameter from the absorption spectra for all the glasses reflects its nature as ionic nature and the results are presented in Table 1. Experimental energies are presented in Table 2.



Fig.1 Vis absorption spectrum of Dy³⁺ ions doped LBWBD1-5 glasses

The oscillator strengths of the observed energy levels were evaluated using J-O theory (Judd BR et al, 1962), (Ofelt GS, 1962). The low values of deviation obtained in the least–square fitting procedure to determine J-O intensity parameters indicate the best-fit between the experimental and calculated oscillator strengths. The experimental and

	LBWBD1		LBW	LBWBD2		LBWBD3		LBWBD4		BD5
Level	f _{exp}	f_{cal}	f _{exp}	f_{cal}	f _{exp}	f _{cal}	f _{exp}	f _{cal}	f _{exp}	f _{cal}
⁶ H _{11/2}	0.744	0.929	0.744	0.952	0.893	1.148	0.818	0.987	0.744	0.862
${}^{6}F_{11/2}$	5.951	5.927	5.058	5.032	4.277	4.244	4.909	4.887	5.158	5.142
${}^{6}F_{9/2}$	1.637	1.662	1.612	1.639	1.551	1.584	1.480	1.503	1.488	1.504
${}^{6}F_{7/2}$	2.232	0.064	2.256	0.072	2.430	0.098	1.930	0.076	1.785	0.061
${}^{6}F_{5/2}$	1.115	0.615	1.289	0.704	1.736	0.974	1.208	0.744	0.867	0.594

Table 3: Experimental and calculated band intensities (× 10-6) and rms deviation of Dy3+: LBWBD 1-5 glasses

Table 4: Judd-Ofelt intensity parameters Ω_{λ} ($\lambda = 2, 4, 6$) (× 10⁻²⁰ cm⁻²) Dy³⁺: LBWBD 1-5 glasses

			Glass		
Parameter	LBWBD1	LBWBD2	LBWBD3	LBWBD4	LBWBD5
Ω_2	5.837	5.160	5.375	5.690	5.952
Ω_4	1.213	0.992	0.177	0.691	1.182
Ω_6	1.279	1.526	2.373	1.743	1.447
Ω_4/Ω_6	0.949	0.650	0.075	0.397	0.817
$\Omega_{2+}\Omega_{4+}\Omega_6$	8.329	7.678	7.926	8.125	8.581

oscillator strengths obtained from JO theory are listed in Table 3.

The phenomenological J-O parameters for Dy³⁺ ions in LBWBD 1-5 glasses are presented in Table 4 which are comparable to phosphate glass systems (SurendraBabu S et al, 2009), (Ofelt GS et al, 1962), (A. Amarnath Reddy et al, 2011) and more for fluoride glass systems (Duan Z et al, 2007), (Pisarska J et al, 2009). It is known that the intensities and positions of the absorption transitions of rare earth ions are sensitive to the local environment of RE ions sites occupied within the glass matrix (Reisfeld R et al, 1977). Therefore these parameters provide critical information on the nature of bond between RE ions to the surrounding ligands. According to Reisfeld and Jorgensen, one of the J-O parameters Ω_2 is most sensitive to local structure and to host composition. It is known that Ω_2 increases with increase in covalence. Relatively larger Ω_2 value indicates that the Dy-O bond in LBWBD 1-5 glasses is predominantly of covalent in nature (Jayasimhadri M et al, 2006). Hypersensitive transition shows strong dependence up on the value of Ω_2 . In our present study ${}^{\mathrm{b}}\mathrm{H}_{15/2} \rightarrow {}^{\mathrm{b}}\mathrm{F}_{11/2}$ is a hypersensitive transition whose magnitude of oscillator strength is much more than the other transitions in all the glass systems studied. The J-O parameters determined from the absorption spectra are used along with refractive indices to predict the important radiative properties such as transition probabilities (A), branching ratios (β_r) and radiative lifetimes (τ_R) for certain excited states of Dy^{3+} ions. The radiative transition probability (A) for a transition can be calculated from the following equation (SurendraBabu S et al, 2009) is reported in literature.

The total radiative transition probability (A_T) involving all the transitions from an excited state to lower states is given by the sum of transition probability A_T = Σ A_R. The predicted radiative lifetime (τ_R) for certain excited states of LBWBD 1-5 glass systems are in the following order, ${}^{6}H_{13/2} {>}^{6}H_{9/2} {>}^{6}H_{11/2} {>}^{6}F_{5/2} {>}^{6}F_{11/2} {>}^{4}F_{9/2}$.

The experimental spectral intensity (f_{exp}) of the absorption bands are obtained using area method is evaluated following equation (K. K. Mahato et al, 2005).

$$f_{cal} = 4.32 \times \int \varepsilon(\nu) d\nu$$

 $\varepsilon(\nu)$ is the molar extinction coefficient. The Judd –Ofelt intensity parameter Ω_{λ} are obtained from these experimental spectral intensities using least square fitting approach along with the matrix elements reported in literature (W. T .Carnall et al, 1977). The experimental and calculated band intensities of LBWBD 1-5 glasses are reported in the Table 3 in the following equation (SurendraBabu S et al, 2009).

$$f_{cal} = \frac{8\pi m c \nu}{3h(2J+1)} \frac{(n^2+2)^2}{9n} \sum_{\lambda=2,4,6} \Omega_{\lambda} (\Psi J \| U^2 \| \Psi J')^2$$

It is observed that in all the five glasses the value of Ω_2 is higher.

The higher values obtained for the environment sensitive and covalency related parameter (Reisfeld R et al, 1977) in all glasses studied suggests more or less similar asymmetry provided around rare earth ion site. It is also worth to note that Ω_2 is also more sensitive to the local structure and in turn strongly depends on the hyper sensitive transition ${}^{6}\text{H}_{15/2} \rightarrow {}^{6}\text{F}_{11/2}$. The variation in intensities of hypersensitive transition ${}^{6}\text{H}_{15/2} \rightarrow {}^{6}\text{F}_{11/2}$ in all LBWBD1-5 glasses studied possess the following order in their spectral intensities LBWBD1 > LBWBD5 > LBWBD2 > LBWBD4 > LBWBD3.

The same spectral intensity variation along with variation in Ω_2 parameters in all glasses indicates that LBWBD1 glass is more symmetric and LBWBD2 glass is less symmetric. The trend of J-O parameters in the present work is found to be in the $\Omega_2 > \Omega_6 > \Omega_4$ order for all glass matrices. The magnitude variation trend of Ω_6 parameter in all the glasses studied is as follows.

LBWBD1>LBWBD5>LBWBD2>LBWBD4>LBWBD3

It appears that the rigidity of glass matrix LBWBD1 is more compared to the other glasses under study. It is evident that the magnitudes of Ω_2 and Ω_6 Parameters of first glass show higher values. It is revealed that this glass possesses higher symmetry and large rigidity.

Transi	tion	LBWBD	1	LBWBD	2	LBWBD	3	LBWBD	94	LBWBD	5
		S'ed	А	S'ed	А	S' _{ed}	А	S' _{ed}	А	S' _{ed}	А
${}^{4}F_{9/2}$	${}^{6}F_{1/2}$	0.049	0	0.040	0	0.007	0	0.028	0	0.047	0
	${}^{6}F_{3/2}$	0.063	0	0.066	0	0.075	0	0.066	0	0.067	0
	${}^{6}F_{5/2}$	3.492	21	3.494	18	3.603	17	3.824	17	4.021	17
	${}^{6}F_{7/2}$	1.048	9	1.018	8	0.943	7	0.969	7	1.090	7
	⁶ H _{5/2}	0.602	6	0.550	5	0.350	3	0.465	4	0.611	5
	⁶ H _{7/2}	2.383	33	2.325	30	2.284	28	2.277	26	2.487	27
	${}^{6}F_{9/2}$	1.222	17	1.055	14	0.650	8	0.936	11	1.222	5
	${}^{6}\text{H}_{9/2}$	2.069	40	1.944	36	2.086	36	2.067	33	2.144	32
	${}^{6}F_{11/2}$	2.801	54	2.555	46	2.582	44	2.697	43	2.876	43
	${}^{6}\text{H}_{11/2}$	6.269	180	5.661	152	6.001	152	6.187	147	6.430	144
	⁶ H _{13/2}	39.28	1740	36.85	1535	41.40	1620	40.29	1480	40.78	1408
	⁶ H _{15/2}	4.470	343	5.109	369	7.278	494	5.62	358	4.963	297
${}^{6}F_{5/2}$	${}^{6}F_{7/2}$	30.82	1	27.33	1	26.39	1	28.89	1	31.37	1
5/2	⁶ H _{5/2}	55.29	7	46.69	6	26.39	1	28.89	1	31.37	1
	${}^{6}\text{H}_{7/2}$	173.8	77	169.7	71	204.6	80	187.4	69	182.9	63
	${}^{6}F_{9/2}$	12.85	6	10.85	5	5.813	2	9.381	4	12.75	5
	⁶ H _{9/2}	213.6	288	189.5	240	191.5	228	205.0	229	217.7	229
	${}^{6}F_{11/2}$	18.02	23	19.13	23	22.66	26	19.56	21	19.39	19
	${}^{6}\text{H}_{11/2}$	43.26	159	42.74	148	39.84	130	40.20	123	45.22	130
	⁶ H _{13/2}	61.97	583	64.33	569	71.24	592	64.16	501	66.08	485
	⁶ H _{15/2}	44.18	1142	52.69	1281	81.97	1873	60.21	1291	49.96	1007
⁶ H _{9/2}	${}^{6}F_{11/2}$	79.98	0	89.27	0	121.6	0	96.68	0	87.94	0
512	⁶ H _{11/2}	241.1	12	217.7	10	224.6	10	234.5	10	247.1	10
	⁶ H _{13/2}	90.41	55	94.15	54	114.4	62	99.32	50	96.87	46
	⁶ H _{15/2}	27.53	105	32.04	115	47.42	160	35.82	113	30.80	92
⁶ F11/2	⁶ H11/2	130.9	6	147.1	7	202.3	9	159.7	6	144.3	5
11/2	⁶ H _{13/2}	299.1	161	291.7	148	329.0	157	309.6	138	313.7	132
	⁶ H _{15/2}	672.1	2200	595.4	1833	564.7	1634	624.3	1695	683.6	1744
бц	⁶ LJ	210.4	10	192.1	16	150.2	12	182.0	14	212.2	15
$n_{11/2}$	п _{13/2} бц	210.4 142.7	19 201	103.1	201	205.2	12	162.0	14	212.2 154.4	13
	$H_{15/2}$	142.7	201	151.5	201	205.2	200	109.4	198	154.4	170
⁶ H _{13/2}	⁶ H _{15/2}	280.6	73	271.6	66	301.0	69	287.0	62	293.5	59

Table 5: Electric dipole line strengths (S'_{ed} cm⁻² x 10⁻²⁰) and radiative probabilities A (s⁻¹) of certain lasing transition of Dy³⁺: LBWBD 1-5 glasses

 $\begin{array}{l} \mbox{Table 7: Emission peak wavelengths } (\lambda_{p,}\mbox{nm}) \mbox{ effective line widths } (\Delta\lambda_{eff}) \mbox{ and stimulated emission cross Sections } \\ (\sigma_e \times \ 10^{-20} \ \mbox{cm}^2) \ \ of \ Dy^{3+} \mbox{: LBWBD 1-5 Glasses} \end{array}$

Transition	LBWBD1 LF			LBWBD	BWBD2 LBWBD3			LBWBD4			LBWBD5				
${}^{4}F_{9/2} \rightarrow$	λ_{p}	$\Delta\lambda_{eff}$	σ_{e}												
⁶ H _{13/2}	559	11.7	1.70	559	13.15	1.60	561	14.40	1.35	579	15.30	1.37	559	11.7	1.70
${}^{6}\mathrm{H}_{13/2}$	487	13.5	0.20	485	12.6	0.29	486	14.40	0.18	487	18.00	0.12	487	13.5	0.20

Table 6: Branching ratios(β) and integrated absorption cross sections ($\sigma_a \ge 10^{-18} \text{ cm}^2$) of the certain lasing transition of Dy³⁺: LBWBD 1-5 glasses

Trai	Transition		LBWBD 1		LBWBD 2		LBWBD 3		BD 4	LBWBD 5	
		β	σ_a	β	σ_a	β	σ_a	β	σ_a	β	σ_a
${}^{4}F_{9/2}$	${}^{6}F_{1/2}$	0.000	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.001
	${}^{6}F_{3/2}$	0.000	0.001	0.000	0.001	0.000	0.001	0.001	0.001	0.000	0.001
	${}^{6}F_{5/2}$	0.009	0.078	0.008	0.067	0.007	0.067	0.069	0.069	0.009	0.070
	${}^{6}F_{7/2}$	0.004	0.024	0.004	0.022	0.003	0.020	0.020	0.010	0.003	0.013
	⁶ H _{5/2}	0.003	0.015	0.002	0.013	0.001	0.008	0.010	0.010	0.003	0.013
	⁶ H _{7/2}	0.013	0.064	0.014	0.061	0.012	0.058	0.056	0.056	0.013	0.059

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	${}^{6}F_{9/2}$	0.007	0.033	0.006	0.028	0.003	0.017	0.023	0.023	0.007	0.029
	${}^{6}\text{H}_{9/2}$	0.016	0.062	0.016	0.057	0.015	0.059	0.057	0.057	0.021	0.077
	${}^{6}F_{11/2}$	0.022	0.084	0.021	0.074	0.018	0.073	0.074	0.074	0.021	0.077
	${}^{6}\text{H}_{11/2}$	0.073	0.215	0.693	0.188	0.063	0.194	0.194	0.194	0.072	0.196
	⁶ H _{13/2}	0.712	1.555	0.693	1.417	0.672	1.546	1.460	1.460	0.706	1.436
	${}^{6}\text{H}_{15/2}$	0.141	0.213	0.167	0.236	0.205	0.327	0.245	0.245	0.149	0.210
${}^{6}F_{5/2}$	⁶ F _{7/2}	0.000	0.150	0.000	0.129	0.000	0.121	0.129	0.129	0.000	0.136
	${}^{6}\text{H}_{5/2}$	0.003	0.444	0.002	0.364	0.001	0.191	0.298	0.298	0.003	0.392
	${}^{6}\text{H}_{7/2}$	0.034	2.087	0.030	1.979	0.027	2.317	2.059	2.059	0.033	1.954
	${}^{6}F_{9/2}$	0.003	0.157	0.002	0.129	0.001	0.067	0.105	0.105	0.002	0.139
	${}^{6}F_{11/2}$	0.010	0.308	0.010	0.371	0.009	0.365	0.306	0.306	0.010	0.295
	⁶ H1/11	0.070	1.051	0.063	1.008	0.044	0.913	0.894	0.894	0.067	0.977
	${}^{6}\text{H}_{13/2}$	0.255	2.058	0.243	2.074	0.202	2.231	1.951	1.951	0.249	1.952
	⁶ H _{15/2}	0.499	2.054	0.547	2.380	0.638	3.596	2.564	2.564	0.158	2.068
⁶ H _{9/2}	${}^{6}F_{11/2}$	0.000	0.014	0.000	0.015	0.000	0.020	0.016	0.016	0.000	0.014
	${}^{6}\text{H}_{11/2}$	0.071	1.000	0.058	0.877	0.044	0.879	0.891	0.891	0.066	0.912
	${}^{6}\text{H}_{13/2}$	0.321	0.859	0.320	0.869	0.267	1.025	0.864	0.864	0.313	0.819
	⁶ H _{15/2}	0.608	0.481	0.640	0.544	0.690	0.782	0.573	0.573	0.620	0.479
${}^{6}F_{11/2}$	${}^{6}\text{H}_{11/2}$	0.003	0.472	0.003	0.515	0.005	0.688	0.527	0.527	0.003	0.463
	⁶ H _{13/2}	0.068	2.411	0.074	2.284	0.087	2.502	2.285	2.285	0.070	2.251
	${}^{6}\text{H}_{15/2}$	0.929	9.888	0.922	8.507	0.908	7.838	8.410	8.410	0.927	8.949
⁶ H _{11/2}	⁶ H _{13/2}	4227	0.938	3396	0.793	3240	0.632	0.743	0.743	2787	0.842
	⁶ H1 _{5/2}	44324	1.585	43398	1.633	68490	2.151	1.723	1.723	31383	1.527

The radioactive properties such as transition probabilities, Total radioactive transition (A_T), radioactive life times (τ_R), branching ratios (β_r) and absorption cross sections σ_a of certain lasing transitions of Dy³⁺: pbo-Bi₂O₃-WO₃-B₂O₃ glass are given in Table 5,6. The measured life times are taken from decay curves shown in Fig. The computed radioactive lifetimes τ_R (μ s) and measured life times are reported in Table 8. The ordering of life time magnitudes in the lasing transitions are as follows for LBWBD1-5 glasses ${}^{6}H_{5/2} {<}^{4}F_{9/2} {<}^{6}F_{11/2} {<}^{6}H_{11/2} {<}^{6}H_{13/2}$.

3.3. Emission Spectra

The emission spectra excited at 575nm for Dy^{3+} : pbo-Bi₂O₃-WO₃-B₂O₃ LBWBD1-5 glasses are shown Fig 2. It is observed that the spectra obtained indicate two intense emission bands ${}^{4}F_{9/2}\rightarrow {}^{6}H_{15/2}$ (487nm), ${}^{4}F_{9/2}\rightarrow {}^{6}H_{13/2}$ (577nm). The other two expected feeble bands at ${}^{4}F_{9/2}\rightarrow {}^{6}H_{11/2}$ (around 665nm), ${}^{4}F_{9/2}\rightarrow {}^{6}H_{9/2}$ (750 nm) approximately due to either poor resolution of instrument or feeble nature of the bands in the present study.







Fig. 3 The decay profiles for the ${}^{4}F_{9/2}$ excited Dy³⁺ ions in LBWBD 1-5 glasses

The ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ transition is considered to lie in the yellow region is a hyper sensitive transition obeying the selection rules $\Delta J = \pm 2$ and $\Delta L = \pm 2$ (S.Tanabe et al, 1992). It is therefore evident that the influence of the matrix on the intensity of the transition. The glasses when excited at 450nm appear to be with yellowish white due to the large yellow to blue intensity ratio. The emission peak wave length (λ_{p}), effective line widths ($\Delta \lambda_{eff}$) and stimulated emission cross sections (σ_{e}) of Dy³⁺: LBWB1-5 glasses are shown in Table 7. It is interesting to note that $\Delta \lambda_{eff}$ for ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ observed is in the following order: LBWBD4>LBWBD3>LBWBD5> LBWBD1>LBWBD2

The small effective line width $\Delta\lambda_{eff}$ for this transition indicates that the transition is sharp compared to the other transitions. The high $\sigma(\lambda_P)$ value and small $\Delta\lambda_{eff}$ values suggests that the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ transition is most potential for lasing action (M.B. Saisudha et al, 2002).

3.5. Decay curve analysis

The decay curves of Dy^{3+} ions were also recorded for different concentrations of Dy^{3+} ion and the life time of

Glass		Trans	itions			$\tau_{\rm R}$		
	${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2} \text{ (Yellow)} \qquad {}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2} \text{ (}$		${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ (Blue)		Y/B	μs	τ_{R} (µs)	η
	$\lambda_p nm$	$\Delta\lambda_{eff} nm$	$\lambda_p nm$	$\Delta\lambda_{eff} nm$				
LBWBD1	559	11.7	487	13.5	1.153	409	303	0.741
LBWBD2	559	13.15	485	12.6	1.149	452	308	0.681
LBWBD3	561	14.40	486	14.40	1.154	415	232	0.559
LBWBD4	579	15.30	487	18.00	1.155	470	213	0.453
LBWBD5	559	11.7	487	13.5	1.190	502	192	0.382

Table 8: Spectral Parameters of Dy³⁺: LBWBD 1-5 glasses

⁴F_{9/2}level have been calculated. Decay curves for yellow bands for 1 mol% Dy³⁺ ion samples are given in Fig. 3. These tabulated in Table 8. The large reduction in lifetime of this level shows the involvement of non-radiative processes at higher concentrations. It would be probably due to the increasing interaction between the Dy–Dy ions (Y. Dwivedi et al, 2009). The measured life time (t_{mes}) of ⁴F_{9/2} fluorescent level could be determined by taking first e-folding times of the decay curves. The quantum efficiency of the excited ⁴F_{9/2} state η is given by equation (V. Venkataramuet at al) $\eta = \frac{\tau_{mes}}{\tau_p}$

3.6. Chromaticity coordinates and white light emission

The LBWBD glasses emit white light at a particular yellow to blue (Y/B) intensity ratio of $({}^{4}F_{9/2} / {}^{6}H_{13/2})/({}^{4}F_{9/2} / {}^{6}H_{15/2})$ emission transitions as given in Table 8. The evaluated chromaticity color coordinates (x, y) are (a) Dy1 (0.32, 0.37), (b) Dy2 (0.32, 0.37), (c) Dy3 (0.33, 0.37), (d) Dy4 (0.32, 0.36), (e) Dy5 (0.33, 0.36), (f) Equal energypoint for LBWBD glasses respectively. These coordinates fall in the white light region of CIE-1931 chromaticity diagram [47] as indicated in Fig. 10. From these results, it is suggested that the titled glasses emit white light under 386 nm excitation wavelength. It is obvious that these coordinates are very close to the standard equal energy white light illumination as observed in the chromaticity diagram.



Figure 4. The CIE chromaticity diagram showing the color coordinates for Dy³⁺ ion doped LBWBD 1-5 glasses

Regarding luminescence data, the chromaticity coordinates (x, y) are deliberate by means of MATLAB

CIE coordinates program. They are indicated in the perimeter of CIE (Commission International edeIEclairage) 1931 chromaticity diagram as shown in the Fig 4 (V. Poli Reddy et al, 2014).

Conclusions

The room temperature HMO glasses with the following $50Pbo+10Bi_2O_3+10WO_3+29B_2O_3+1DY_2O_3$ were synthesized using conventional melt Quenching technique. The physical parameters density, refractive index were evaluated using conventional methods. The spectroscopic parameters were evaluated and reported. The bonding nature for all the glasses (LBWBD1-5 glasses) obtained to be of covalency in nature. The Judd-Ofelt intensity parameters evaluated employed to evaluate emission transitions. The Y/B luminescence ratios obtained from photoluminescence spectra show higher values and LBWBD5 glass can be recommended because of the high Y/B ratio.

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