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Optical properties of Dy^{3+} ions in alkali metal borate glass

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Abstract: ***Dy^{3+} doped alkali metal borate glasses ($68B_2O_3$-$15Na_2O$-$15Li_2O$-$2Dy_2O_3$) are prepared by the conventional melting procedure. Optical absorption and luminescence spectra have been measured at room temperature. Using the Judd – Ofelt (JO) theory, the intensity parameters (Ω_λ, λ = 2,4,6) have been evaluated for BNaLi:Dy^{3+} glass. These intensity parameters are used to predict radiative properties that include electric (S_{ed}) magnetic (S_{md}) dipole line strength, radiative transition probabilities (A_R), lifetime (τ_R), branching ratios (β_R) for the excited levels of Dy^{3+}. In addition, the stimulated emission cross – sections ($\sigma_{\lambda p}$) and integrated emission cross – section (Σ_{ip}) have been predicted for the transitions $^4F_{9/2} \rightarrow {}^6H_J$ (J=15/2,13/2,9/2).***

*Keywords:***alkali metal borate glass, relaxation mechanism**

I. INTRODUCTION

Glasses doped with rare earth (RE) ions are good laser materials as they emit intense radiations in the visible (Vis) and near-infrared (NIR) spectral regions under suitable excitation conditions. Due to the unique structural and physico chemical properties, alkali metal borate glasses doped with RE^{3+} ions have been widely used as laser materials, optical amplifiers, optical memories, optoelectronics and magneto-optical devices [7]. The presence of structurally different borate units in alkali metal borate glasses is favorable for spectroscopic investigations of RE^{3+} ions. These structural differences are usually correlated to chemical composition, type of modifiers and conditions during glass preparation. Low phonon energy glasses doped with Dy^{3+} ions have been studied for optical amplifiers and yellow–green up conversion [8] applications. Special interest has been devoted to Dy^{3+} doped borate glasses with various chemical compositions [9]. Depending upon the host environment, the Dy^{3+} ions emit several emission bands between its f–f transitions [1]. The visible luminescence of the Dy^{3+} ion mainly consists of yellow band at 570–600 nm corresponding to the $^4F_{9/2}$-$^6H_{13/2}$ hypersensitive transition and the blue band at 470–500 nm corresponding to the $^4F_{9/2}$-$^6H_{15/2}$ transition. Dysprosium doped glasses and crystals emit intense discrete radiation in the yellow (570–600 nm) and NIR (1.35 and 3.0 mm) regions that have potential technological applications in commercial displays and telecommunications [10,11]. The intensity of the $^4F_{9/2}$- $^6H_{13/2}$ hypersensitive transition strongly depends on the host, in contrast to a less sensitive $^4F_{9/2}$-$^6H_{15/2}$ transition of Dy^{3+} and results in different yellow to blue luminescence intensity ratios that largely change with concentration and/or glass composition. In this work, we prepared and studied spectroscopic properties of Dy^{3+} ions in alkali metal borate glass. Judd–Ofelt (J-O) theory [3,6] has been used to evaluate intensity parameters Ω_λ by analyzing the absorption spectrum of BNaLi:Dy^{3+} glass, and calculated the radiative transition probabilities, branching ratios, radiative lifetimes of $^4F_{9/2}$ excited level, stimulated emission cross – section for selected. Beside that, the potential application of the BNaLi:Dy^{3+} glass as laser materials is described.

II. EXPERIMENT

Alkali metal borate glass (BNaLi glass) doped with 2.0 mol% of Dy^{3+} are prepared by conventional melt quenching technique. The molar composition of dysprosium doped BNaLi glasses investigated in this work is $68B_2O_3$+$15Na_2O$+$15Li_2O$+$2Dy_2O_3$. High purity chemicals of H_2BO_3, Na_2CO_3, Li_2CO_3 and Dy_2O_3 were used as starting materials. All the above weighed chemicals were well-mixed and heated for 90 min in a platinum crucible at 1050 ^oC in an electric furnace, then cooled quickly to 350 ^oC and annealed at this temperature for 120 min to remove thermal strains. The glass samples were slowly cooled to room temperature, shaped and polished to measure their physical and optical properties. For concentration determination, density measurement was made by Archimede method using xylene as the immersion liquid. Refractive index was measured with an Abbe's refract meter with sodium vapor lamp using 1-bromonaphthalin as the contact liquid. Optical absorption spectra were recorded in the wavelength regions 200 nm – 2500 nm using Varian spectrometer system cary 5E UV - VIS - NIR, with a resolution of 1nm. Fluorescence and excitation spectra were obtained at room temperature using Flourolog-3 Model FL3-22, resolution of 0.3 nm, excitation light xenon (Vehicle).

III. RESULTS AND DISCUSSION

A. *Judd-Ofelt analysis*

Absorption spectra:

Fig 1a and 1b show the absorption spectra of Dy^{3+} ions - doped borate glass in the UV-Vis and NIR regions, respectively. There are thirteen observed absorption peaks at 320, 350, 362, 381, 425, 455 and 470 nm in UV-Vis band and 745, 800, 895, 1090, 1270 and 1675 nm in near-infrared band, which are attributed to transitions from $^6H_{15/2}$ ground state to ($^6P_{3/2}$,$^4M_{17/2}$), $^6P_{7/2}$, ($^4M_{19/2}$,^{4}(D,P)$_{3/2}$), $^6P_{3/2}$, ($^4F_{7/2}$, $^4I_{13/2}$), $^4G_{11/2}$, $^4I_{15/2}$, $^4F_{9/2}$ and $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, ($^6H_{7/2}$, $^6F_{9/2}$), ($^6H_{7/2}$,

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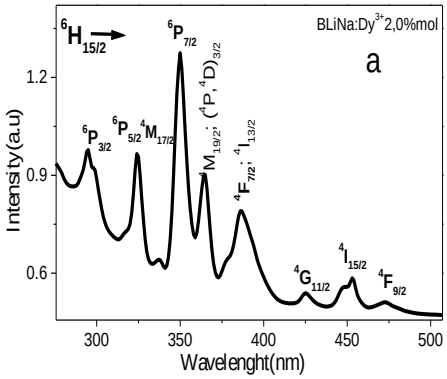
$^6F_{11/2}$), $^6H_{11/2}$ higher excited states in order of increasing wavelength, respectively.



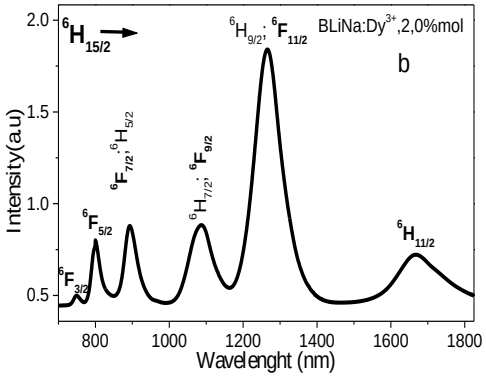


Table 1: Energy transitions (ν), bonding parameters (δ), the experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths for BNaLi:Dy^{3+} glass

Transition $^6H_{15/2}$ →	ν_c (cm^{-1})	ν_{quo} (cm^{-1})	f_{exp} ($\times10^{-6}$)	f_{cal} ($\times10^{-6}$)
$^6H_{11/2}$	5,995	5,850	3.21	3.07
$^6F_{11/2}$,$^6H_{9/2}$	7,898	7,730	16,54	16,57
$^6F_{9/2}$,$^6H_{7/2}$	9,199	9,100	5.97	6,50
$^6F_{7/2}$	11,198	11,000	4.91	5,15
$^6F_{5/2}$	12,468	12,400	3.25	2,36
$^6F_{3/2}$	13,351	13,250	0.39	0,48
$^4F_{9/2}$	21,141	21,100	0.54	0,39
$^4I_{15/2}$	22,075	22,100	1.18	1,04
$^4G_{11/2}$	23,529	23,400	0.29	0,21
$^4F_{7/2}$,$^4I_{13/2}$	25,839	25,800	4.45	1,91
$^4M_{19/2}$,$^4(D,P)_{3/2}$,$^6P_{3/2}$	27,397	27,400	3.9	3,50
$^6P_{7/2}$	28,571	28,550	9.12	7,89
$^6P_{3/2}$,$^4M_{17/2}$	30,864	30,892	3.14	2,02
	$\bar{\beta}=1.0063$; $\delta=-0.62$		rms = 1.09×10^{-6}	

The transition from $^6H_{15/2}$ to the levels $^6H_{9/2}$ is hypersensitive in nature for Dy^{3+} ions which obeys the selection rule $|\Delta J| \le 2$, $\Delta S = 0$ and $|\Delta L| \le 2$ and any local structural change may sharply effect the position and intensity of this transition [1]. The energy of these absorption transitions of Dy^{3+} ion in BNaLi glass host are also compared with Dy^{3+} -diluted acid solution (aquo-ion) system [2] and shown in Table 1.

Nephelauxetic effect- Bonding parameter

The bonding parameter (δ) is defined as $\delta=\left[\left(1-\bar{\beta}\right)/\bar{\beta}\right]\times100$ [1,4,5], where $\bar{\beta}=(\sum\beta)/n$ and β (nephelauxetic ratio) = ν_c/ν_a, ν_c and ν_a are energies of the corresponding transitions in the complex and aquo–ion [2], respectively, and n is refers to the number of levels that are used to compute $\bar{\beta}$ values. Depending on the field environmental, the bonding parameter (δ) can be received the positive or negative value indicating covalent or ionic bonding. In our sample, the values of $\bar{\beta}$ and δ bonding parameter are 1.0063, - 0.62, respectively. Thus, the bonding of Dy^{3+} ions with the local host is ionic bonding.

Oscillator strengths and JO parameters

The experimental (f_{exp}) and calculation oscillator strengths (f_{exp}) of absorption bands are determined using Eq [1,3,6]:

$$f_{exp}=4{,}318.10^{-9}\int\alpha(\nu)d\nu \qquad (1)$$

$$f_{ed}=\frac{8\pi^2mc}{3h\bar{\lambda}(2J+1)}n\left(\frac{n^2+2}{3n}\right)^2\sum_{\lambda}\Omega_{\lambda}\left\|U^{(\lambda)}\right\|^2 \qquad (2)$$

Where α is molar extinction coefficient at energy ν (cm^{-1}). The $\alpha(\nu)$ values can be calculated from absorbance A by using Lambert – Beer's law: $A = \alpha(\nu)Cd$, C is concentration [dim: L^{-3}; units: $moll^{-1}$], d is the optical path length [dim: L; units: cm]. n is the refractive index of the material, J is the total angular momentum of the ground state, Ω_λ are the JO intensity parameters and $\left\|U^{\lambda}\right\|^2$ are the squared doubly reduced matrix of the unit tensor operator of the rank λ = 2,4,6 are calculated from intermediate coupling approximation for a transition $\left|\psi J\right\rangle\rightarrow\left|\psi' J'\right\rangle$. These reduced matrix elements did not nearly depend on host matrix as noticed from earlier studies [2]. All thirteen absorption bands have been analyzed using JO theory and were least squared fitted to yield the best fit values for the JO parameters. Table 2 compared the JO intensity parameters obtained for BNaLi:Dy^{3+} glass with some of the reports on systems:Dy^{3+} [8-11].

The table 2 shows the values of Ω_2 and Ω_6 in BNaLi glass is larger than that of the different hosts. The characteristic feature of the Ω_2 is that it is sensitive to the local environment of the RE^{3+} ions and is often related with the asymmetry of the coordination structure, polarizability of ligand ions or molecules and bonding nature [8-11].

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Table 2: The JO parameters of Dy^{3+} ions doped various hosts

Host matrix	$\Omega_2 01\cdot(^{02-}\mu\chi^2)$	$\Omega_4 01\cdot(^{02-}\mu\chi^2)$	$\Omega_6 01\cdot(^{02-}\mu\chi^2)$	Ω_4/Ω_6	Ref.
BLiNa:Dy^{3+} glass	16,28	5,78	5.32	1,08	Present
L6B:Dy^{3+} glass	12,83	3,47	3,43	1,01	[8]
PKBFA:Dy^{3+} glass	10,41	2,29	2,07	1,10	[11]
NaLTB:Dy^{3+} glass	9,86	3,39	2,41	1,41	[9]
NaLTB:Dy^{3+} glass	9,25	2,87	2,29	1,25	[9]
LiLTB:Dy^{3+} glass	8,75	2,62	2,07	1,26	[9]
PKMAF:Dy^{3+} glass	7,04	1,73	1,57	1,10	[10]

The larger of Ω_2 parameter in BNaLi:Dy^{3+} glass than other hosts can be attributed to lower symmetry of the coordination structure surrounding the RE^{3+} ion. The Ω_6 parameter related to the rigidity of the medium in which the RE^{3+} ions are embedded. Rigid matrices shown low values for the Ω_6 parameter [1]. The larger of Ω_6 parameter in BNaLi:Dy^{3+} glass than other hosts suggests that the rigidity of the surrounding environment Dy^{3+} in BnaLi glass is lower than other hosts. The spectroscopic quality factor $\chi = \Omega_4/\Omega_6$, is one of the important lasing characteristic parameters which is used to predict the stimulated emission in any active medium. The Dy^{3+} doped glass hosts possessing spectroscopic quality factors in the range 0.42–1.92 are the good candidates for laser active media [9]. The observed values of χ in BNaLi:Dy^{3+} glass is 1.08, this suggests that BNaLi:Dy^{3+} glass is good material for various optical devices.

B. Fluorescence spectra and radiation properties

From the JO parameters, the radiative properties such as the electric (S_{ed}) and magnetic (S_{md}) dipole line strengths, the radiative transition rates (A_R), radiative lifetime (τ_R), branching ratios (β_R) were calculated for excited levels $^4F_{9/2}$. The results are showed in table 3. As shown in Fig. 2, which illustrates the emission spectrum using the 365 nm excitation wavelength of xenon lamp source, 4 emission bands at 481, 575, 664 and 755 nm which are attributed to transitions from $^4F_{9/2}$ to $^6H_{15/2}$, $^6H_{13/2}$, $^6H_{11/2}$ and $^6H_{9/2}$ respectively, of Dy^{3+}ions. But among of them, the yellow (Y) band (575 nm) corresponds to the hypersensitive transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$, and the blue (B) band (481 nm) corresponds to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition are the dominant bands in the emission spectrum. The intensity ratio of yellow emission to blue emission (Y/B) of the Dy^{3+}ions dependents on the asymmetry of the ligand. With the BNaLi:Dy^{3+}, the Y/B ratio is 1.27 and higher than other hosts [9-11]. The higher value of Y/B indicates that the higher degree of covalence between dysprosium and oxygen ions.

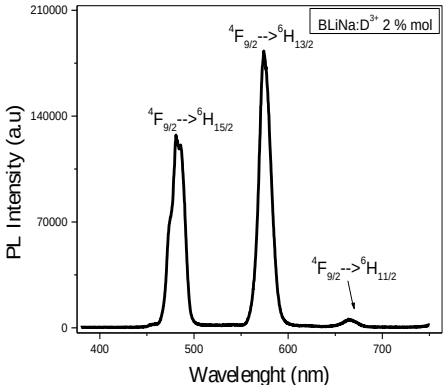

Fig. 2. The emission spectrum of BNaLi:Dy^{3+} glass

From the JO parameters and refractive index, the radiative properties such as the electric (S_{ed}) and magnetic (S_{md}) dipole line strengths, the radiative transition rates (A_R), radiative lifetime (τ_R), branching ratios (β_R) were calculated for $^4F_{9/2}$ excited levels. The results are showed in table 3.

Table 3. Transition energies (ν), radiative transition probabilities (S_{ed}, S_{md}, A and A_T), radiative lifetime (τ_R) and branching ratios (β_R) for excited levels

Transition $^4F_{9/2} \rightarrow$	ν (cm^{-1})	S_{ed} ($\times 10^{-4}$ $^0cm^2$)	S_{md} ($\times 10^{-4}$ $^0cm^2$)	A (s^{-1})	β_R (%)
$^6F_{1/2}$	7,291	0.05	0	0.19	0.01
$^6F_{3/2}$	7,902	0.04	0	0.19	0.01
$^6F_{5/2}$	8,556	2.59	0	17.1	0.71
$^6F_{7/2}$	9,946	1.03	0.4	11.3	0.47
$^6H_{5/2}$	10,900	0.61	0	8.11	0.34
$^6H_{7/2}$	11,963	2.3	0.18	40.6	1.68
$^6F_{9/2}$	12,066	1.07	0.16	19.41	0.8
$^6H_{9/2}$	13,258	2.09	0.02	51	2.11
$^6H_{11/2}$	13,398	1.61	1.65	44.6	1.84
$^6H_{11/2}$	15,209	4.34	0.31	159.2	6.59
$^6H_{13/2}$	17,628	28.9	0	1620	66.81
$^6H_{15/2}$	21,182	4.64	0	448	18.5
	$A_T(^4F_{9/2}) = 2420\ s^{-1}$; $\tau_R(^4F_{9/2}) = 413\ \mu s$				

From the emission spectrum of BNaLi:Dy^{3+} glass, the emission peak positions (λ_p), effective line width ($\Delta\lambda_{eff}$), measured branching ratios (β_{exp}), stimulated emission cross –

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section $\sigma(\lambda_p)$ and integrated emission cross – section (Σ_{if}) were calculated for $^4F_{9/2} \rightarrow {}^6H_J$ (J = 15/2, 13/2, 11/2, 9/2) transitions. The results are displayed in Table 4.

Table 4. Emission peak positions (λ_p), effective line width ($\Delta\lambda_{eff}$), radiative transition probabilities (A), branching ratios (β_{exp}), stimulated emission cross – section $\sigma(\lambda_p)$ and integrated emission cross – section (Σ_{if}) for $^4F_{9/2} \rightarrow {}^6H_J$ transitions of Dy^{3+} in BLiNa glass.

$^4F_{9/2}$ →	$\Delta\lambda_{eff}$ (nm)	A_r (s^{-1})	$\sigma(\lambda_p)$(× 10^{-22} cm^2)	Σ_{if}(× 10 $^{-18}$ cm)	β_R (%)	
					exp	cal
$^6H_{9/2}$	22.3	44.6	2.4	0.12	1.24	1.84
$^6H_{11/2}$	25.9	159.21	6,5	0.38	4,62	6.59
$^6H_{13/2}$	16.4	1620	60,1	2.99	56,32	66.81
$^6H_{15/2}$	18.5	448	7,2	0.58	37.82	18.5

In general, the luminescence branching ratio is a critical parameter to the laser designer, because it characterizes the possibility of attaining stimulated emission from any specific transition. In this work, the predicted branching ratio of $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition get a maximum value and be 66.8 % where as the measured ratio is 56.32 %. Thus there is a good agreement between experimental and calculated branching ratios. The integrated emission cross–section, Σ_{if}, was an important parameter when considering the laser emission of the material. When the integrated emission cross–section is greater than 10^{-18} cm, laser emission is probable [13]. In our case, with the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition, the integrated emission cross – section is 2.99×10^{-18} cm. The stimulated emission cross – section $\sigma(\lambda_p)$, which is an another of the most important parameter that affects the potential laser performance and its value signifies rate of energy extraction from the lasing material. It is found that $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition exhibits maximum $\sigma(\lambda_p)$ (60.1×10^{-22} cm^2). The large values of branching ratio, integrated emission cross – section and stimulated emission cross section suggest that the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition can give rise to lasing action.

IV. CONCLUSION

Dy^{3+}doped alkali metal borate glasses were prepared by melt quenching technique and investigated through the absorption and photoluminescence spectra. The negative value of bonding parameter δ shows that the bonding of Dy^{3+} ions with the local host is ionic bonding. JO theory has been applied to determine the intensity parameters by analyzing the absorption spectra. The larger of Ω_2 parameter and Y/B ratio in BNaLi:Dy^{3+} glass than other hosts can be attributed to lower symmetry of the coordination structure surrounding the RE^{3+} ion. The large of the spectroscopic quality (χ) suggests that BNaLi:Dy^{3+} glass is good material for various optical devices. The large values of branching ratio, integrated emission cross – section and stimulated emission cross section suggest that the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition can give rise to lasing action.

REFERENCES

[1] Christane Görller, Walrand and K. Binnemans "Spectral intensities of f – f transition", Handbook on the Physics and Chemistry of Rare Earths. Vol.25, pp.101 – 252.

[2] Carnall W.T., Fields P.R., and Rajnak K, "Electronic Energy Levels in the Trivalent Lanthanide Aquo Ions. I. Pr^{3+}, Nd^{3+}, Pm^{3+}, Sm^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, and Tm^{3+}", J. Chem. Phys, Vol. 49, No. 10, pp. 4424-4442, 1968.

[3] Judd BR, "Optical absorption intensities of rare earth ions", Phy Rev; 127:750–61, 1962.

[4] Jørgensen. CK, Reisfeld. R, "Judd–Ofelt parameters and chemical bonding", J Less-Common Met, pp.93-107, No.12, 1983.

[5] Lin H, Pun EYB, Wang X, Lin X, "Intense visible fluorescence and energy transfer in Dy^{3+},Tb^{3+},$Sm^{3+}$and Eu^{3+}doped rare-earth borate glasses", J Alloys Compd, No.390, pp. 197–201, 2005.

[6] Ofelt GS, "Intensities of crystal spectra of rare-earth ions", J Chem Phys 1962; 37:511–20. fluoroborate glasses. Opt Mater, Vol. 15, pp.65–79, 2000.

[7] Tripathi G, Rai VK, Rai SB, "Spectroscopy and up conversion of Dy^{3+} doped in sodium zinc phosphate glass", Spectrochim Acta A, No. 62: 1120–4, 2005.

[8] Tanabe S, Kang J, Hanada T, Soga N, "Yellow/blue luminescence of Dy^{3+} doped borate glasses and their anomalous temperature variations", J Non-Cryst Solids, 239:170–5, 1998.

[9] S.A. Saleema, B.C. Jamalaiah, M. Jayasimhadri, A. Srinivasa Rao, Kiwan Jang, L. Rama Moorthy. "Luminescent studies of Dy3+ ion in alkali lead tellurofluoroborate glasses", Journal of Quantitative Spectroscopy & Radiative Transfer, pp. 78–84 2011.

[10] Surendra Babu S, Babu P, Jayasankar CK, Siewers W, Wortmann G, "Optical spectroscopy of Dy^{3+}: phosphate and fluorophosphates glasses". Opt Mater, 31: 624–31, 2009.

[11] Sardar DK, Bradley WM, Yow RM, Gruber JB, Zandi B, "Optical transitions and absorption intensities of Dy^{3+} ($4f^9$) in YSGG laser host", J Lumin, 106, pp.195–203, 2004.

[12] Yang Z, Li B, He F, Luo L, Chen W, "Concentration dependence of Dy^{3+}1.3 mm luminescence in Ge–Ga–Sb–Se glasses", J Non-Cryst Solids, 354: pp.1198–2000, 2008.

[13] Wang D., Guo Y., Wang Q., Chang Z., Liu J., Luo J., "Judd-Ofelt analysis of spectroscopic properties of Tm^{3+} in K_2YF_5 crystal", J. Alloy. Compd 474, pp. 23-25, 2009.