

## Structural and Optical Studies on Dy<sup>3+</sup> Doped Alkali Zinc Fluoroborate Glasses for White Light Stimulation

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### Abstract

The trivalent Dy<sup>3+</sup> ions doped Alkali zinc fluoroborate glasses with the chemical composition (40-x)B<sub>2</sub>O<sub>3</sub>+20ZnO+20Na<sub>2</sub>O+20NaF+xDy<sub>2</sub>O<sub>3</sub> (x = 0.1, 0.3 and 1.0 wt%) were prepared by melt quenching technique. Spectroscopic properties of the prepared glasses were characterized through XRD, FTIR, UV-VIS-NIR absorption spectra and Photoluminescence spectra. The bonding parameters ( $\beta$  and  $\delta$ ) and the oscillator strength were calculated from the absorption spectrum. The negative values of bonding parameters reveal the ionic nature of the prepared glasses. The luminescence spectra exhibit two visible <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>15/2</sub> (Blue) and <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>13/2</sub> (Yellow) transitions. The Judd-Ofelt intensity parameters ( $\Omega_2$ ,  $\Omega_4$ ,  $\Omega_6$ ) were determined from the absorption spectra to investigate the nature of metal-ligand bond and symmetry around the Dy<sup>3+</sup> ion site. The radiative properties bandwidth ( $\Delta\lambda_{\text{eff}}$ , nm), transition probability (A), branching ratios ( $\beta_R$ ) and stimulated emission cross-section ( $\sigma_p^E \times 10^{-22}$  cm<sup>2</sup>) for the <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>15/2</sub> and <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>13/2</sub> transitions were calculated. The CIE chromaticity co-ordinates were calculated for all glass samples. The emission colors were found to lie in white light region for prepared glasses and thus can be used for bright white LED's.

**Keywords:** Glasses, Hypersensitive transitions, Bonding parameter, Emission, White light emission

### 1. Introduction

Spectroscopic studies of rare earth (RE) ions doped materials draw much attention due to their potential

applications in the field of photonics [1,2]. Rare earth (RE)-doped glasses have attracted great attention because of their capability to control the properties like refractive index, density, structure and optical absorption. Among the oxide glasses borate (B<sub>2</sub>O<sub>3</sub>) is a good glass former, good transparency, good RE ion solubility and thermal stability [3]. Boron is normally established in the glasses in the form of triborate and tetraborate units. The Dy<sup>3+</sup> ion is an attractive laser ion with optical transitions in the visible as well as infrared region due to its intricate energy level structure. Dy<sup>3+</sup> ion exhibits strong luminescence in the Blue and yellow spectral region suitable for stimulation of white light where the emission intensities strongly depend upon the concentration of Dy<sup>3+</sup> ions, glass matrix and excitation energies. The present work reports the structural and optical studies on Dy<sup>3+</sup> doped alkali zinc fluoroborate glasses for white LED applications.

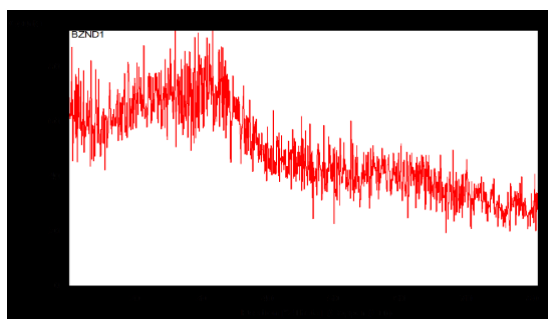
### 2. Experimental technique

The Dy<sup>3+</sup> doped alkali zinc fluoroborate glasses were prepared by conventional melt quenching technique followed by the literature [1,2]. The X-ray diffraction of prepared glasses were recorded using XPERT-PRO X-ray Diffractometer with CuK $\alpha$  radiation. The FTIR spectra were recorded using Perkin-Elmer in the range of 400 to 4000 cm<sup>-1</sup> for prepared glass samples. The UV-VIS-NIR spectra were measured at room temperature using JASCO V-750 spectrometer for all glasses. The luminescence

studies were carried out using Perkin Elmer LS45 Fluorescence spectrometer.

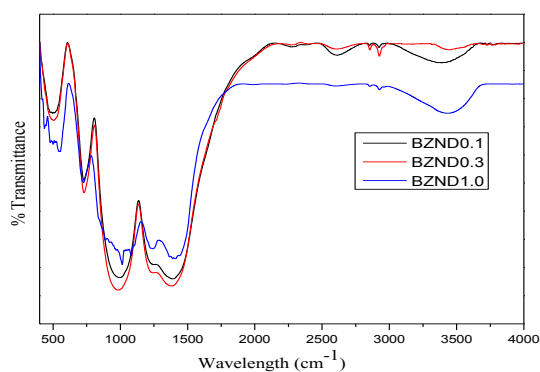
### 3. Results and discussion

#### 3.1. Structural analysis



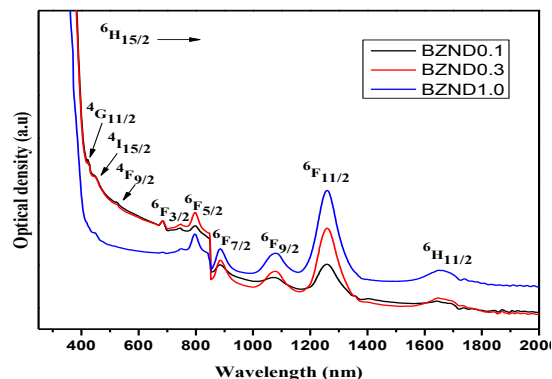
**Figure 1.** XRD pattern of Dy<sup>3+</sup>:BZND1.0 alkali zinc fluoroborate glass

The XRD pattern of the Dy<sup>3+</sup>:BZND1.0 glass as shown in Figure 1. It exhibits broad pattern diffuse at lower scattering angle structural disorder which is confirmed the amorphous nature of the prepared glasses [4]. The fundamental stretching units of various functional groups have been identified through FTIR spectra and is shown in Figure 2. The peak appeared at 3437 cm<sup>-1</sup> is owing to O-H stretching vibrations. The formation of Hydrogen bonding is confirmed at 2924 and 2857 cm<sup>-1</sup>. The broad band at 1377 cm<sup>-1</sup> reveals B-O stretching vibrations of BO<sub>3</sub> unit. The band position at around 1007 cm<sup>-1</sup> is stretching of BO<sub>4</sub> group. The narrow peak at 724 cm<sup>-1</sup> is because of B-O-B bending vibrations. The Zn-O metal oxide bond formation is ensured by the peak appeared at 485 cm<sup>-1</sup> [1-3].



**Figure 2.** Infrared spectra of Dy<sup>3+</sup>: alkali zinc fluoroborate glass

#### 3.2. Absorption spectra



**Figure 3.** Absorption spectra of Dy<sup>3+</sup>: alkali zinc fluoro borate glasses

The absorption spectra of Dy<sup>3+</sup> doped alkali zinc fluoroborate glasses are recorded in the region 200–2000 nm and are shown in Figure 3 which are similar to the other reported Dy<sup>3+</sup>-doped glasses [2,5]. The optical absorption spectra exhibit several inhomogeneously broadened bands due to f-f transitions from the ground state <sup>6</sup>H<sub>15/2</sub> to various excited state. Among the all transitions <sup>6</sup>H<sub>15/2</sub>→<sup>6</sup>F<sub>11/2</sub> is the hypersensitive transition which obey the selection rules |ΔS| = 0, |ΔL| ≤ 2 and |ΔJ| ≤ 2 possess higher intensity and also Dy<sup>3+</sup> ions is sensitive in local environment. From the observed band positions (in cm<sup>-1</sup>), nephelauxetic ratio (β) and bonding parameter (δ) of the Dy<sup>3+</sup> doped fluoroborate glasses are calculated and listed in table 1 along with aqua-ion [2]. The bonding parameters were identified as covalent / ionic depending on the positive or negative sign of δ. It is observed from the table 1 that, the negative values indicates the ionic nature.

**Table 1.** Observed band positions (in  $\text{cm}^{-1}$ ),  $\bar{\beta}$  and  $\delta$  of the prepared  $\text{Dy}^{3+}$  doped BZND $x$  glasses

${}^6\text{H}_{15/2}$	BZND0.1	BZND0.3	BZND1.0	[2]
${}^4\text{G}_{11/2}$	23697	23697	23810	23400
${}^4\text{I}_{15/2}$	22222	22124	22222	22100
${}^4\text{F}_{9/2}$	21231	21186	21097	21100
${}^6\text{F}_{3/2}$	13477	13369	13405	13250
${}^6\text{F}_{5/2}$	12531	12531	12563	12400
${}^6\text{F}_{7/2}$	11312	11287	11287	11000
${}^6\text{F}_{9/2}$	9328	9294	9276	9100
${}^6\text{F}_{11/2}$	7949	7937	7949	7700
${}^6\text{H}_{11/2}$	6024	6039	6031	5850
$\bar{\beta}$	1.0125	1.0164	1.0204	-
$\delta$	-1.8299	-1.6150	-1.9999	-

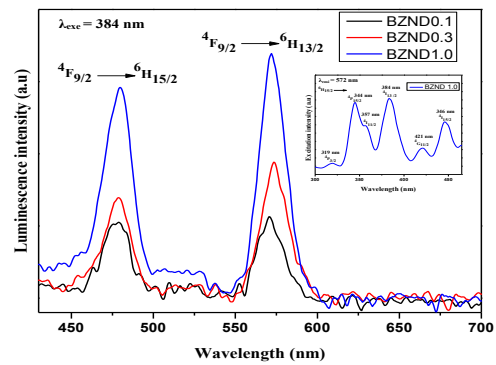
**Table 2.** Experimental and calculated oscillator strengths ( $\times 10^6$ ) of the  $\text{Dy}^{3+}$  doped alkali Zinc fluoroborate glasses

${}^6\text{H}_{15/2}$ $\rightarrow$	BZND0.1		BZND0.3		BZND1.0	
	$f_{\text{exp}}$	$f_{\text{cal}}$	$f_{\text{exp}}$	$f_{\text{cal}}$	$f_{\text{exp}}$	$f_{\text{cal}}$
${}^4\text{G}_{11/2}$	0.575	0.058	0.433	0.030	0.314	0.029
${}^4\text{I}_{15/2}$	0.506	0.209	0.563	0.183	0.369	0.142
${}^4\text{F}_{9/2}$	0.543	0.080	0.201	0.071	0.188	0.050
${}^6\text{F}_{3/2}$	0.589	0.085	0.341	0.0823	0.268	0.056
${}^6\text{F}_{5/2}$	0.996	0.449	0.457	0.4367	0.436	0.297
${}^6\text{F}_{7/2}$	1.270	1.080	0.945	0.9374	0.741	0.668
${}^6\text{F}_{9/2}$	1.467	1.539	1.096	1.1045	0.833	0.859
${}^6\text{F}_{11/2}$	3.872	3.841	2.391	2.3888	2.581	2.571
${}^6\text{H}_{11/2}$	0.386	0.631	0.506	0.5354	0.348	0.428
N	9		9		9	
$n_d$	1.567		1.569		1.567	
$\Omega_2$	3.701		2.382		2.747	
$\Omega_4$	1.647		1.393		0.785	
$\Omega_6$	1.087		1.055		0.715	
$\sigma$	0.369		0.209		0.160	

The experimental ( $f_{\text{exp}}$ ) and calculated ( $f_{\text{cal}}$ ) oscillator strengths of the absorption bands of individual transition are calculated from the absorption spectra of the relative areas under the absorption spectra and presented in table 2 [2]. The Judd–Ofelt [6,7] intensity parameters ( $\Omega_\lambda$ ) ( $\lambda = 2, 4, 6$ ) are determined from the experimental oscillator strength values ( $f_{\text{exp}}$  values) by using least square fit procedure. The obtained J–O intensity parameters are as follows for all the prepared glasses. However, the  $\Omega_2$  values are found to be higher than the  $\Omega_4$  and  $\Omega_6$  intensity parameter values in the prepared glasses. Thus lower of  $\Omega_4$  and  $\Omega_6$  values suggests that

the structural network will be more open and becoming high rigid due to the formation of NBO which reflects the deformation of  $\text{BO}_4$  unit to  $\text{BO}_{3+1}$  or  $\text{BO}_3$  structural units and vice versa. The trend  $\Omega_2 > \Omega_4 > \Omega_6$  has been observed for all the prepared glasses in the experiment.

### 3.3. Emission and Excitation spectra



**Figure 4.** Luminescence spectra of  $\text{Dy}^{3+}$ :Zinc fluoroborate glasses [inset shows the excitation spectrum of BZND1.0 glass]

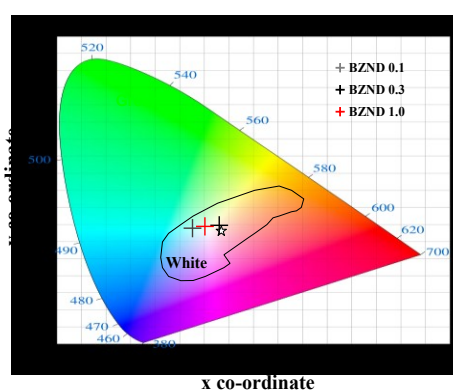
Inset Figure 4 shows excitation spectrum of BZND0.1 glass. The excitation spectra contains of six bands owing to the electronic transitions at 319, 344, 357, 384, 421 and 446nm corresponding to  ${}^4\text{P}_{3/2}$ ,  ${}^6\text{P}_{7/2}$ ,  ${}^4\text{I}_{11/2}$ ,  ${}^4\text{I}_{13/2}$ ,  ${}^4\text{G}_{11/2}$  and  ${}^4\text{I}_{15/2}$  transitions respectively. Among these transitions, the intensity of the excitation band observed at 384 nm corresponding to the  ${}^6\text{H}_{15/2} \rightarrow {}^4\text{I}_{13/2}$  transition is found to be higher when compared to other transitions and the same is used as an excitation wavelength to record the emission spectra of the prepared glasses. The luminescence spectra of  $\text{Dy}^{3+}$  doped alkali zinc fluoroborate glasses were recorded in the region 400–700nm and is shown in Figure 4. Luminescence spectra exhibit two emission bands at 480nm and 572nm corresponding to  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$  (Blue) and  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$  (Yellow) transitions respectively. From the emission spectra, the intensity of peaks increases

with increase of Dy<sup>3+</sup> ion concentration. The yellow emission (electric dipole) transition possesses higher intensity than the blue emission (magnetic dipole) transitions for all prepared glasses. The hypersensitive in nature and its intensity of electric dipole transition is strongly influenced by the ligand field around the Dy<sup>3+</sup> ion site [10]. Appropriate combination of the dominant emission transitions corresponding to the blue (<sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>15/2</sub>) and yellow (<sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>13/2</sub>) bands exhibit white light emission [6]. The <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>13/2</sub> emission transition possess higher intensity compared to the other transitions thus indicates the higher asymmetry possessed by the Dy<sup>3+</sup> ions with its surrounding ligands. The radiative properties such as peak wavelength ( $\lambda_p$ , nm), the effective bandwidth ( $\Delta\lambda_{eff}$ , nm), transition probability (A), experimental branching ratios ( $\beta_R$ ) and stimulated emission cross-section ( $\sigma_p^E \times 10^{-22}$  cm<sup>2</sup>) for the <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>15/2</sub> and <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>13/2</sub> transitions were calculated from luminescence spectra and presented in table 3. It is observed from table 3 that, the branching ratio of the <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>13/2</sub> emission transition is found to be higher than the other emission transitions and follows the trend as <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>13/2</sub> > <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>15/2</sub> > <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>11/2</sub> uniformly for all the prepared glasses. Among the prepared glasses BZND0.1 (21.602) higher stimulated emission cross-section values. The higher stimulated emission cross-section is suggested for low-threshold, high gain applications and are utilized to obtain continuous wave laser action.

**Table 3.** Bandwidth ( $\Delta\lambda_{eff}$ , nm), transition probability (A), branching ratios ( $\beta_R$ ) and stimulated emission cross-section ( $\sigma_p^E \times 10^{-22}$  cm<sup>2</sup>) for the <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>15/2</sub> and <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>13/2</sub> transitions of the Dy<sup>3+</sup>doped alkali zinc fluoroborate glasses

Parameters	BZND0.1	BZND0.3	BZND1.0	
<sup>4</sup> F <sub>9/2</sub> → <sup>6</sup> H <sub>15/2</sub>	$\lambda_p$	479	479	480
	$\Delta\lambda_{eff}$	12.348	14.489	14.105
	A	97.11	92.28	61.05
	$\sigma_p^E$	2.237	1.802	1.233
	$\beta_R$ (cal)	0.152	0.180	0.571
	$\beta_R$ (exp)	0.503	0.506	0.474
<sup>4</sup> F <sub>9/2</sub> → <sup>6</sup> H <sub>13/2</sub>	$\lambda_p$	571	573	572
	$\Delta\lambda_{eff}$	9.967	8.315	10.113
	A	374.80	276.79	263.29
	$\sigma_p^E$	21.602	19.476	14.965
	$\beta_R$ (cal)	0.589	0.541	0.132
	$\beta_R$ (exp)	0.497	0.494	0.526

### 3.5. White Light Stimulation



**Figure 5.** CIE chromaticity co-ordinates of Dy<sup>3+</sup>: alkali zinc fluoro borate glasses

The CIE chromaticity co-ordinates were calculated for all glass samples and present in Table 4. The emission colors were found to lie in white light region for prepared glasses as shown Figure 5 and thus can be used for bright white LED's [12-14]. Among the prepared glasses, it is observed that BZND 0.3 glass (0.32795, 0.34813) is closer to the standard (0.33, 0.33) equal energy white light illuminate.

**Table 4.** The Y/B ratio (yellow to blue) and chromaticity co-ordinates (x, y) values for the Dy<sup>3+</sup>doped alkali zinc fluoroborate glasses.

Glasses	Y/B ratio	chromaticity co-ordinates		Ref
		x	y	
BZND0.1	1.192	0.2737	0.3398	Present work
BZND0.3	1.198	0.3279	0.3481	
BZND1.0	1.191	0.2989	0.3451	
0.5DPTFB	0.590	0.311	0.302	[9]
LSBP0.1D y	1.871	0.380	0.397	[10]
TZPPN	0.88	0.38	0.43	[11]

#### 4. Conclusion

Dy<sup>3+</sup> doped alkali zinc fluoroborate glasses were prepared by melt quenching technique and their structural and spectroscopic behavior were discussed and reported. The XRD pattern confirms the amorphous nature of the prepared glasses. The FTIR studies exhibit the B-O stretching vibrations of BO<sub>3</sub> units. The bonding parameter studies reveal the ionic nature of the metal-ligand bond in the title glasses and the ionicity decreases with the increase in Dy<sup>3+</sup> ions. The obtained J-O intensity parameters are as follows  $\Omega_2 > \Omega_4 > \Omega_6$  for all the prepared glasses. However, the  $\Omega_2$  values are found to be higher than the  $\Omega_4$  and  $\Omega_6$  intensity parameter values in the prepared glasses. Through the luminescence spectra, the peak wavelength, effective bandwidth, experimental branching ratios ( $\beta_R$ ) and stimulated emission cross-section ( $\sigma_p^E \times 10^{-22} \text{ cm}^2$ ) calculated for  $^4F_{9/2} \rightarrow ^6H_{15/2}$  and  $^6H_{13/2}$  transitions and the results were reported. The prepared glasses exhibit emission in visible region. These results demonstrate that the present glass system is one of the promising material for visible laser and white light stimulation applications.

#### References

[1] M. Vijayakumar, K. Marimuthu, J. Alloys Compds. 629 (2015) 230–241.

- [2] R.T. Karunakaran, K. Marimuthu, S. Surendra Babu, S. Arumugam, Physica B, 404 (2009) 3995–4000.
- [3] J.N. Ayuni, M.K. Halimah, Z.A. Talib, H.A.A. Sidek, W.M. Daud, A.W. Zaidan, A.M. Khamiru, Mat. Sci. Engg. 17 (2011) 012027.
- [4] M. Jayasimhadri, Kiwan Jang, Ho Sueb Lee, Baojiu Chen, Soung-Soo Yi, Jung-Hyun Jeong, J. Appl. Phys. 106 (2009) 013105.
- [5] I. Arul Rayappan, K. Maheshvaran, S. Surendra Babu, K. Marimuthu, Phys. Status Solidi A, 209 (2012) 570–578.
- [6] B.R. Judd, Phys. Rev. 127 (1962) 750.
- [7] G.S. Ofelt, J. Chem. Phys. 37 (1962) 511
- [8] L. Vijayalakshmi, V. Naresh, B.H. Rudramadevi, S. Buddhudu, Inter. J. Engg. Sci. 4 (2014) 19–25.
- [9] S.Arunkumar, G.Venkataiah, K.Marimuthu, Molecular and Biomolecular Spectroscopy (2014), doi: <http://dx.doi.org/10.1016/j.saa.2014.10.067>.
- [10] R. Vijayakumar, G. Venkataiah, K. Marimuthu Journal of Alloys and Compounds (2015), doi: 10.1016/j.jallcom.2015.08.219.
- [11] Journal of Quantitative Spectroscopy & Radiative Transfer 134(2014)55–63 Kamel Damak, El Sayed Yousef, Christian Rüssel, Ramzi Maâlej.
- [12] K. Swapna, Sk. Mahamuda, A. Srinivasa Rao, M. Jayasimhadri, T. Sasikala, L. Rama Moorthy, Journal of Luminescence 139 (2013) 119–124.
- [13] P. Babu, C.K. Jayasankar Optical Materials 15 (2000) 65.
- [14] C.R. Kesavulu, C.K. Jayasankar Materials Chemistry and Physics 130 (2011) 1078– 1085.