Enhancement of Emission Intensity in Dy\textsuperscript{3+}-Doped ZnO/ZnF\textsubscript{2} Phosphoborate Glasses for W-LED Materials

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Abstract. Presently, white light emitting diodes (W-LEDs) were be used to substitute for conventional incandescent and fluorescent lamps due to their advantages; thus, it gets attention to create Dy\textsuperscript{3+}-doped zinc phosphoborate glasses for enhancing better lightness. In this research, the replacing of ZnO by ZnF\textsubscript{2} in 49B\textsubscript{2}O\textsubscript{3}:30P\textsubscript{2}O\textsubscript{5}:(20-x)ZnO:xZnF\textsubscript{2}:1Dy\textsubscript{2}O\textsubscript{3} glasses, 0 \leq x \leq 20 mol\% were prepared by melt quenching method and investigated through optical absorption and photoluminescence properties. The absorption results can be used for calculating the Judd-Ofelt (JO) intensity parameters (\(\Omega\lambda\), \(\lambda = 2, 4\) and \(6\)) and led to predicting the stimulated emission in present glasses. The trend of JO parameters is found to be \(\Omega_2 > \Omega_4 > \Omega_6\) for all glasses. Nevertheless, replacing of ZnF\textsubscript{2} does not affect position and intensity of optical absorption of Dy\textsuperscript{3+}-doped glasses, whereas the observed blue (481 nm), yellow (573 nm) and red (662 and 752 nm) emission intensities of photoluminescence spectra rise with ZnF\textsubscript{2} contents; the emission intensity at 573 nm for 20ZnF\textsubscript{2} show the highest and was higher than 20ZnO around 1.6 times. The emission color of Dy\textsuperscript{3+}-doped zinc phosphoborate glasses has been evaluated with CIE 1931 chromaticity diagram. The results revealed that all glasses emit white light. Hence, these glasses may be suitable candidate for using in W-LED and lighting materials.

1. Introduction
In former times, human known to use the other lighting such as lighting from sun, ignite. Up to now, the scientists have invented lighting devices, namely incandescent and white light emitting diodes (W-LEDs). However, the marketing trend of W-LEDs are better than incandescent [1-3] because of their better luminous efficiency, longer lifetime, excellent reliability, energy saving, eco-friendly, solidity, fast switching, small size, color tenability and good color rendering index [4-6]. From those properties, W-LEDs can be used for room lighting, automotive headlights, solid state lasers, biological labeling, temperature sensors, solar cells and backlighting of liquid crystal displays [7]. Normally, W-LEDs are manufactured by the combination of the YAG:Ce\textsuperscript{3+} phosphors and coupling a blue chip (InGaN) or ultraviolet (AlGaN) LEDs. Nevertheless, the rate of phosphors and blue chip coated on the chip are the result of poor white light efficiency [10]. Moreover, the color rendering index is bad owing to the lack of red light [8-10]. To overcome this drawback, it is necessary to enhance new materials which could emit bright white light by suitable excitation. Rare-earth ions (RE\textsuperscript{3+}) doped glasses are remarkable materials due to their properties comprise easy to fabricate adjustable size and shape, inexpensive cost,
transparent in visible region (no grain boundaries), better thermal stability and high doping concentrations of RE$^{3+}$ ions [11-12]. Additionally, unique RE$^{3+}$ ions in glasses involve the 4f-4f and 4f-5d electronic transitions which cause high luminescence efficiencies, sharp absorption and emission lines because of the shielding by 5s and 5p orbitals [13-14]. Similarly, the selection of host glasses is important factor as the phonon energies of host glasses are determination the luminescence efficiency [15]. Dy$^{3+}$-doped zinc phosphoborate glasses gets attention for enhancing better lightness of W-LEDs. Phosphate glasses are host glasses which have phonon energies around 1200 cm$^{-1}$ [16]. It gains important due to their pros that low melting point temperature, low optical dispersion, high transparency, high thermal expansion coefficient and wide glass formation range [17-19]. On the other hand, the cons of phosphate glasses is theirs hygroscopic nature [20]. Therefore, the borate glasses are mixed in phosphate glasses for solving this problem. Borate glasses are good glass formers because of their higher bond strength, lower cation size, smaller heat of fusion, lower melting point, high optical transparency and larger forming ability [21-22]. Even though borate glasses show various advantages, it has large phonon energies around 1400 cm$^{-1}$ owing to stretching vibrations of network forming oxide. However, this problem can be solved when mixed with phosphate glasses [23-24]. In order that enhance the glass quality [25], optical performance [26] and luminescence properties [27], the zinc oxide (ZnO) has been added in glass matrix. However, ZnO was substituted by ZnF$_2$ which was studied in this work due to its removal the hydroxyl group (OH$^{-}$) [28].

Among of RE$^{3+}$ ions, dysprosium ions (Dy$^{3+}$) have attracted much attention which plays a role in W-LEDs and lighting materials. Normally, Dy$^{3+}$ ions showed three emission bands in visible range including the blue (485 nm, $^{4}F_{9/2}$→$^{4}H_{15/2}$), yellow (575 nm, $^{4}F_{9/2}$→$^{4}H_{11/2}$) and red (665 nm, $^{4}F_{9/2}$→$^{4}H_{11/2}$) emission [29-30]. At an appropriate yellow to blue (Y/B) intensity ratio, Dy$^{3+}$ ions can emit white light emission and led to generate W-LEDs materials [31]. To get the maximum emission from Dy$^{3+}$-doped glasses, the concentration of Dy$^{3+}$ ions at 1.00 mol% was used in this work due to optimum concentration [32].

In this work, the physical, optical absorption and photoluminescence properties of the replacing of ZnO by ZnF$_2$ in Dy$^{3+}$-doped zinc phosphoborate glasses were investigated. From optical absorption spectrum, the oscillator strengths and Judd-Ofelt (JO) parameter have been evaluated and are used to predict radiation properties of Dy$^{3+}$ ions in glass matrix.  

2. Experimental details

Dy$^{3+}$-doped zinc phosphoborate glasses of composition 49B$_2$O$_3$ : 30P$_2$O$_5$ : (20-x) ZnO : xZnF$_2$ : 1Dy$_2$O$_3$ glasses, 0 ≤ x ≤ 20 mol% were prepared by melt quenching method at a temperature 1200 °C for 3 hours using a alumina crucible. Then the melts were quickly poured into a preheated stainless steel mould and anneal at 500 °C for 3 hours before cool down to room temperature. The chemical composition of zinc phosphoborate glasses were shown in Table 1.

### Table 1. Chemical composition of glasses.

| Glass ID | Glass composition (mol%) |
|----------|------------------------|
| ZPB1     | 49B$_2$O$_3$ : 30P$_2$O$_5$ : 20ZnO : 0ZnF$_2$ : 1Dy$_2$O$_3$ |
| ZPB2     | 49B$_2$O$_3$ : 30P$_2$O$_5$ : 15ZnO : 5ZnF$_2$ : 1Dy$_2$O$_3$ |
| ZPB3     | 49B$_2$O$_3$ : 30P$_2$O$_5$ : 10ZnO : 10ZnF$_2$ : 1Dy$_2$O$_3$ |
| ZPB4     | 49B$_2$O$_3$ : 30P$_2$O$_5$ : 5ZnO : 15ZnF$_2$ : 1Dy$_2$O$_3$ |
| ZPB5     | 49B$_2$O$_3$ : 30P$_2$O$_5$ : 0ZnO : 20ZnF$_2$ : 1Dy$_2$O$_3$ |

The densities (ρ) were measured by Archimedes’s method which using water as working liquid at room temperature. All glasses were operated for 5 times. The molar volumes were calculated from densities result as equation:
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\[ V_m = \frac{M_T}{\rho} (\text{cm}^3 / \text{mol}) \quad (1) \]

Where \( V_m \) is molar volume of glasses, \( M_T \) is total molecular weight of glass and \( \rho \) is density of glasses. The refractive indexes were carried on by abbe refractometer and using mono bromonaphthalene (C_{10}H_{7}Br) as a contact liquid. The absorption spectra of glasses were measured using UV-VIS-NIR spectrophotometer (Shimadzu, UV3600) in the range of 340-1900 nm at room temperature. The emission spectra measurements were record by using a fluorescence spectrophotometer (Cary Eclipse) with xenon lamp as a light source.

The experiment \( (f_{\text{exp}}) \) and calculated \( (f_{\text{cal}}) \) oscillator strength of a transition starting from the ground state of a Dy^{3+} ion can be determined from the optical absorption spectra by the expression [33]

\[ f_{\text{exp}} = 4.32 \times 10^{-9} \int \varepsilon(v) dv \]

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

where \( \varepsilon(v) \) is the molar absorptivity at wavenumber \( v (\text{cm}^{-1}) \), \( n \) is the refractive index of medium, \( J \) is the total angular momentum of the ground state, \( \Omega_\lambda \) (\( \lambda = 2, 4 \) and 6) are Judd-Ofelt (JO) intensity parameters and \( ||U^J||^2 \) are the doubly reduced matrix elements of the unit tensor operator of the rank \( \lambda = 2, 4 \) and 6. They are calculated from the intermediate coupling approximation for the transition, \( \psi J \rightarrow \psi' J' \).

The radiation transition probability \( (A) \) for a transition \( \psi J \rightarrow \psi' J' \) can be evaluated from the follow relation:

\[ A(\Psi J, \Psi' J') = A_{\text{ed}} + A_{\text{md}} \quad (4) \]

where \( A_{\text{ed}} \) and \( A_{\text{md}} \) are the electric and magnetic-dipole radiative transition probabilities, respectively and are given by,

\[ A_{\text{ed}} = \frac{64\pi^4 v^3}{3h(2J+1)} \frac{n(n^2+2)^2}{9} S_{\text{ed}} \]

\[ A_{\text{md}} = \frac{64\pi^4 v^3}{3h(2J+1)} n^3 S_{\text{md}} \quad (5) \]

where \( S_{\text{ed}} \) and \( S_{\text{md}} \) are the electric and magnetic dipole line strengths, respectively, which can be calculated from the following expressions:

\[ S_{\text{ed}} = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda (\Psi J || U^J || \Psi' J')^2, \]

\[ S_{\text{md}} = \frac{e^2 h^2}{16\pi^2 m^2 c^2} (\Psi J || L + 2S || \Psi' J')^2 \quad (6) \]

The total radiative transition probability \( (A_T) \) for an excited state is given as the sum of the \( A(\Psi J, \Psi' J') \) terms calculated over all the terminal states,

\[ A_T(\Psi J) = \sum \Psi J, \Psi' J' \quad (7) \]
The fluorescence branching ratio ($\beta$) corresponding to the emission from as excited $\Psi J$ level to a lower $\Psi' J'$ level can be obtained from the transition probabilities by using, 

$$\beta_R(\Psi J, \Psi' J') = \frac{A(\Psi J, \Psi' J')}{A_R(\Psi J)}$$

(8)

The stimulated emission cross-section is an important JO parameter which is calculated by using the follow equation:

$$\sigma(\lambda_p) = \frac{\lambda_p^4}{8\pi cn^2\Delta\lambda_{eff}} A_R$$

(9)

where $\lambda_p$ is the transition peak wavelength, $c$ is velocity of light, $n$ is refractive index of glasses and $\Delta\lambda_{eff}$ is its effective line width derived by dividing the area of the emission band by its average height.

The emission color of Dy$^{3+}$-doped zinc phosphoborate glasses were characterized in the frame of the chromaticity color coordinates under exciting wavelength at 347 nm. The correlated color temperature (CCT) is calculated by McCamy approximate formula for investigation the quality of light source.

3. Results and discussion

Table 2 showed the molecular weights, densities, molar volumes and refractive indexes of Dy$^{3+}$-doped zinc phosphoborate glasses. Normally, the densities depend on the molecular weight of glasses so the densities of glasses were increased with the addition of ZnF$_2$ replace ZnO. Since the molecular weight of ZnF$_2$ (Mw = 103.3768 g/mol) is higher than ZnO (Mw = 81.3790 g/mol). The increasing of densities pointed to a change in the geometrical and coordination configuration, structural softening and the dimension of interstitial space of glass [34]. The molar volumes of Dy$^{3+}$-doped zinc phosphoborate glasses were also increase with substitution ZnO by ZnF$_2$ because of the fluoride ion of ZnF$_2$ created non-bridging oxygens (NBOs) and F sites in glass which substitutes for bridging oxygens (BOs) ions [35]. The refractive indexes of Dy$^{3+}$-doped zinc phosphoborate glasses were increased since speed of light in glasses travel slowly when densities increase as equation,

$$n = \frac{c}{v}$$

(10)

where $n$ is refractive index of glasses, $c$ is speed of light in vacuum (3 x 10$^8$ m/s) and $v$ is speed of light in glass (m/s). The trend of densities and molar volumes of Dy$^{3+}$-doped zinc phosphoborate glasses with the concentration of ZnF$_2$ were shown in Figure 1 whereas the refractive indexes were shown in Figure 2.

Table 2. Molecular weight, density, molar volume and refractive index of Dy$^{3+}$-doped glasses.

| Glass ID | Molecular weight (g/mol) | Density (g/cm$^3$) | Molar volume (cm$^3$/mol) | Refractive index |
|----------|------------------------|-------------------|---------------------------|-----------------|
| ZPBD1    | 96.7018                | 2.5998±0.0005     | 37.1959±0.0012            | 1.6544±0.0002   |
| ZPBD2    | 97.8017                | 2.6169±0.0002     | 37.3731±0.0010            | 1.6552±0.0001   |
| ZPBD3    | 98.9016                | 2.6315±0.0001     | 37.5837±0.0021            | 1.6561±0.0002   |
| ZPBD4    | 100.0015               | 2.6469±0.0002     | 37.7806±0.0013            | 1.6572±0.0001   |
| ZPBD5    | 101.1014               | 2.6553±0.0001     | 38.0753±0.0014            | 1.6580±0.0001   |
Figure 1. The densities and molar volumes of Dy$^{3+}$-doped glasses with the concentration of ZnF$_2$.

Figure 2. The refractive index of Dy$^{3+}$-doped glasses with the concentration of ZnF$_2$.

Figure 3 showed the optical absorption of Dy$^{3+}$-doped zinc phosphoborate glasses. The absorption spectra exhibited eleven bands, located at 347, 386, 425, 451, 472, 752, 796, 892, 1086, 1258, 1671 nm and were found to originate from a transition ground state $^6$H$_{15/2}$ to $^6$P$_{7/2}$, $^4$F$_{7/2}$, $^4$G$_{11/2}$, $^4$I$_{15/2}$, $^4$F$_{9/2}$, $^6$F$_{5/2}$, $^6$F$_{7/2}$, $^6$F$_{9/2}$, $^6$F$_{11/2}$ and $^6$H$_{11/2}$, respectively [36]. The transition $^6$H$_{15/2}$ → $^6$P$_{7/2}$ showed the highest band in UV-visible range when compared to the other transition peaks that were observed. Whereas the transition $^6$H$_{15/2}$ → $^6$F$_{11/2}$ promoted the highest band in near-infrared (NIR) region and was hyperresponsive transition as selection rule $\Delta S = 0$, $|\Delta L| < 2$, $|\Delta J| < 2$ [37]. The absorbance of Dy$^{3+}$-doped zinc phosphoborate glasses was seen nearly. It indicated that the substitution of ZnO by ZnF$_2$ is not effect to absorbance of glasses. The optical absorption intensity is expressed in term of oscillator strengths and led to calculate the experiment, calculated oscillator strength and JO parameter ($\Omega_2$, $\Omega_4 = 2, 4$ and $6$) as expression (2) and (3). The experimental oscillator strength ($f_{exp}$) values were evaluated from the absorption bands, while the calculated oscillator strength ($f_{cal}$) values of Dy$^{3+}$-
doped zinc phosphoborate glasses were calculated from JO theory. Both of oscillator strength values were promoted in Table 3 and the JO intensity parameters were shown in Table 4.

![Absorbance spectrum of Dy\textsuperscript{3+} doped glasses.](image)

**Figure 3.** The optical absorption of Dy\textsuperscript{3+}-doped zinc phosphoborate glasses.

**Table 3.** Experimental ($f_{\exp} \times 10^{-6}$), calculated ($f_{\text{cal}} \times 10^{-6}$) oscillator strengths and JO parameters ($\Omega_{\lambda}, \lambda = 2, 4$ and 6) of various transitions of Dy\textsuperscript{3+} ions originating from $^6\text{H}_{15/2}$ level.

| Transition $^6\text{H}_{15/2} \rightarrow$ | Wavelength (nm) | ZPBD1 | ZPBD2 | ZPBD3 | ZPBD4 | ZPBD5 |
|------------------------------------------|-----------------|-------|-------|-------|-------|-------|
| $^6\text{P}_{3/2}$ | 347 | 9.74 | 9.90 | 13.05 | 13.26 | 8.40 | 8.50 | - | - | - | - |
| $^6\text{F}_{3/2}$ | 386 | 7.30 | 7.82 | 4.47 | 4.40 | 5.19 | 5.78 | 4.25 | 4.96 | 4.91 | 4.48 |
| $^6\text{G}_{11/2}$ | 425 | 1.77 | 1.70 | 0.58 | 0.64 | 0.29 | 0.17 | 0.29 | 0.45 | 0.58 | 0.74 |
| $^6\text{I}_{15/2}$ | 451 | 4.39 | 4.05 | 1.54 | 1.51 | 1.28 | 1.09 | 1.05 | 1.24 | 2.42 | 2.69 |
| $^6\text{F}_{5/2}$ | 472 | 1.18 | 1.68 | 0.23 | 0.13 | 0.23 | 0.72 | 0.72 | 0.55 | 0.47 | 0.40 |
| $^6\text{F}_{7/2}$ | 572 | 1.98 | 1.25 | 0.73 | 0.52 | 1.69 | 1.07 | 0.75 | 1.23 | 0.75 | 1.13 |
| $^6\text{F}_{9/2}$ | 796 | 4.81 | 4.80 | 3.86 | 0.93 | 4.14 | 4.65 | 3.59 | 3.74 | 4.41 | 4.70 |
| $^6\text{F}_{11/2}$ | 892 | 10.90 | 12.48 | 10.43 | 12.97 | 7.86 | 7.13 | 9.09 | 9.41 | 9.76 | 9.23 |
| $^6\text{H}_{15/2}$ | 1086 | 25.01 | 25.60 | 14.91 | 14.89 | 12.18 | 12.62 | 17.25 | 17.73 | 15.38 | 15.63 |
| $^6\text{H}_{11/2}$ | 1258 | 55.62 | 53.83 | 37.06 | 37.53 | 45.08 | 45.26 | 50.32 | 50.67 | 45.19 | 45.41 |
| $^6\text{H}_{9/2}$ | 1671 | 7.82 | 7.05 | 6.57 | 6.04 | 9.01 | 9.05 | 7.81 | 7.04 | 6.22 | 6.04 |

| $\Omega_2$ | 27.59 | 27.01 | 26.22 | 25.46 | 25.31 |
| $\Omega_4$ | 18.32 | 17.05 | 16.78 | 15.62 | 14.87 |
| $\Omega_6$ | 9.47 | 8.95 | 8.92 | 8.17 | 8.04 |
Table 4. The Judd-Ofelt intensity parameters ($\Omega_i \times 10^{20}$ cm$^2$), trend of ZPBD1, ZPBD2, ZPBD3, ZPBD4 and ZPBD5 glasses and for some of the other reported Dy$^{3+}$-doped glasses.

| Glass ID     | $\Omega_2$ | $\Omega_4$ | $\Omega_6$ | Trend | References |
|--------------|------------|------------|------------|-------|------------|
| ZPBD1        | 27.59      | 18.32      | 9.47       | $\Omega_2 > \Omega_4 > \Omega_6$ | This work |
| ZPBD2        | 27.01      | 17.05      | 8.95       | $\Omega_2 > \Omega_4 > \Omega_6$ | This work |
| ZPBD3        | 26.22      | 16.78      | 8.92       | $\Omega_2 > \Omega_4 > \Omega_6$ | This work |
| ZPBD4        | 25.46      | 15.62      | 8.17       | $\Omega_2 > \Omega_4 > \Omega_6$ | This work |
| ZPBD5        | 25.31      | 14.87      | 8.04       | $\Omega_2 > \Omega_4 > \Omega_6$ | This work |
| PKBAFD10     | 12.34      | 2.67       | 2.30       | $\Omega_2 > \Omega_4 > \Omega_6$ | [42]      |
| KFP05Dy      | 20.47      | 1.00       | 0.43       | $\Omega_2 > \Omega_4 > \Omega_6$ | [43]      |
| L7BD         | 13.28      | 4.39       | 4.46       | $\Omega_2 > \Omega_6 > \Omega_4$ | [44]      |
| BiNFBD1      | 5.53       | 1.56       | 1.66       | $\Omega_2 > \Omega_6 > \Omega_4$ | [45]      |
| NbFSDy10     | 10.05      | 1.37       | 2.16       | $\Omega_2 > \Omega_6 > \Omega_4$ | [46]      |
| PbPKANDy10   | 11.74      | 2.64       | 2.86       | $\Omega_2 > \Omega_6 > \Omega_4$ | [47]      |
| PKAZFDy      | 14.11      | 3.07       | 1.95       | $\Omega_2 > \Omega_4 > \Omega_6$ | [48]      |
| GGA-0.8      | 14.17      | 3.19       | 2.01       | $\Omega_2 > \Omega_4 > \Omega_6$ | [49]      |

From Table 4 presented The Judd-Ofelt intensity parameters ($\Omega_i \times 10^{20}$ cm$^2$), trend of ZPBD1, ZPBD2, ZPBD3, ZPBD4 and ZPBD5 glasses and for some of the other reported Dy$^{3+}$-doped zinc phosphoborate glasses. Generally, the JO parameters provide information on the ligand between Dy$^{3+}$ ions and surrounding bonding [38]. The $\Omega_2$ is involved to covalence of the ligand bond and structural change whereas $\Omega_4$ and $\Omega_6$ are involved with the long range effects and are strongly influenced by the vibrational levels associated with the central Dy$^{3+}$ ions bound to the ligand atoms [39-40]. In this work, the $\Omega_2$ decreased when substituted ZnO by ZnF$_2$ because the F$^-$ ions have higher electronegativity about 4 in Pauling scales, so the Dy$^{3+}$-F$^-$ bond has the small covalency ($\delta < 0$) [41]. For the trend of JO parameters, the present glasses follow as $\Omega_2 > \Omega_4 > \Omega_6$ that similar with PKBAFD10 [42], KFP05Dy [43], PKAZFDy [48] and GGA-0.8 [49] glasses. The trend of $\Omega_2 > \Omega_4 > \Omega_6$ indicated the similar site around Dy$^{3+}$ ions, which may can be a basis for good host glasses for optical applications [50]. Furthermore, the JO parameters along with photoluminescence spectra were used to predict radiation properties of Dy$^{3+}$ ions in glass matrix.

The emission spectra of Dy$^{3+}$-doped zinc phosphoborate glasses were measured in visible range from 400 to 800 nm under the excitation at wavelength 347 nm as shown in Figure 4. It exhibited the strong peak at 481 nm ($^4$F$\rightarrow$ $^6$H$\frac{15}{2}$, blue), 573 nm ($^4$F$\rightarrow$ $^6$H$\frac{13}{2}$, yellow), 662 nm ($^4$F$\rightarrow$ $^6$H$\frac{11}{2}$, red) and 752 nm ($^4$F$\rightarrow$ $^6$H$\frac{9}{2}$, red) [37]. Among of four transitions, the transition $^4$F$\rightarrow$ $^6$H$\frac{15}{2}$ is magnetic dipole (MD) which hardly varies with the crystal field around Dy$^{3+}$ ions. While the transition $^4$F$\rightarrow$ $^6$H$\frac{11}{2}$ is electric dipole (ED) and related with hypersensitive transition with the selection rule ($|\Delta L| \leq 2$ and $|\Delta J| \leq 2$). It is strongly effect by the environment [51]. In general, the ratio intensity between ED and MD transitions has been used to evaluate the symmetry of the ligand field environment of Dy$^{3+}$ ions. For this work, the ED transition intensity is greater than MD transition, indicated that more asymmetry the nature in glass [52]. The emission intensity of Dy$^{3+}$-doped zinc phosphoborate glasses increases when substituted ZnO by ZnF$_2$. Since the fluoride ions of ZnF$_2$ react with the OH group to form HF and cause decrease phonon energies, reduce non-radiative (NR) decay and enhance radiative emission [13]. Comparing the emission intensity at 573 nm, ZPBD5 glass showed the highest and was higher than ZPBD1 around 1.6 times. The comparative intensity of transition $^4$F$\rightarrow$ $^6$H$\frac{11}{2}$ under exciting wavelength at 347 nm was shown in Figure 5. While Figure 6 shows the partial energy level diagram consist of the absorption from $^4$H$\frac{9}{2}$ ground state to excited state and the emission from $^4$F$\rightarrow$ $^4$H$\frac{15}{2}$ to $^4$H$\frac{15}{2}$ of Dy$^{3+}$-doped zinc phosphoborate glasses. The radiative transition probability (A$\rightarrow$),
branching ratio ($\beta_R$) and also stimulated emission cross-section for $^{4}F_{9/2} \rightarrow ^{6}H_{13/2}$ transition of Dy$^{3+}$-doped zinc phosphoborate glasses were calculated by emission results along with the JO theory. Normally, the radiative transition probability is implied to the larger opportunity to achieve better laser action. The branching ratio gives datum about laser designer since it can discuss the possibility of achieving stimulated emission from any specific transition [53]. The predicted radiative transition probabilities ($A_R$, s$^{-1}$), stimulated emission cross section ($\sigma_{em}(\lambda) \times 10^{-21}$ cm$^2$) and branching ratio ($\beta_R$) for the $^{4}F_{9/2} \rightarrow ^{6}H_{13/2}$ transition of Dy$^{3+}$-doped zinc phosphoborate glasses were shown in Table 5. In this work, the experiment and calculated branching ratio values were higher than 50% of total transition peaks. It indicated that good branching ratio and led to lasing power of a transition in glass matrix [41]. The stimulated emission cross-section is an important JO parameter which is calculated by using the follow equation (9). The stimulated emission cross-section ($\sigma_{em}(\lambda) \times 10^{-21}$ cm$^2$) values of ZPBD1, ZPBD2, ZPBD3, ZPBD4 and ZPBD5 glasses were 6.82, 9.26, 10.00, 11.39 and 12.51 ($\times 10^{-21}$) cm$^2$, respectively, and higher than other report as shown in Table 5. The $\sigma_{em}(\lambda)$ value of Dy$^{3+}$-doped zinc phosphoborate glasses increase when substituted ZnO by ZnF$_2$. It showed that ZPBD5 were suitable to utilize as lighting materials.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** The emission spectra of Dy$^{3+}$-doped zinc phosphoborate glasses.
Figure 5. The comparative intensity of transition $^4F_{9/2} \rightarrow ^6H_{13/2}$ under exciting wavelength at 347 nm.

Figure 6. The partial energy level diagram consist of the absorption and emission of Dy$^{3+}$-doped zinc phosphoborate glasses.
Table 5 The predicted radiative transition probabilities ($A_R$, $s^{-1}$), stimulated emission cross-section ($\sigma_{em}(\lambda) \times 10^{21}$ cm$^2$) and branching ratio ($\beta_R$) for the $^4F_{9/2} \rightarrow ^6H_{13/2}$ transition of Dy$^{3+}$-doped zinc phosphoborate glasses and for some of the other reported Dy$^{3+}$-doped glasses.

| Glass ID | $A_R$ | $\sigma_{em}(\lambda)$ | $\beta_R$ | References |
|----------|-------|-------------------------|-----------|------------|
| ZPBD1   | 3230  | 6.82                    | 0.57      | This Work  |
| ZPBD2   | 3270  | 9.26                    | 0.64      | This Work  |
| ZPBD3   | 3425  | 10.00                   | 0.66      | This Work  |
| ZPBD4   | 3494  | 11.39                   | 0.66      | This Work  |
| ZPBD5   | 3618  | 12.51                   | 0.67      | This Work  |
| BTD0.5A | 952   | 6.01                    | 0.64      | [54]       |
| G2 glass| 1636  | 6.25                    | 0.66      | [37]       |
| PKAlCaF Dy10 | 1159 | 4.77                   | 0.29      | [39]       |
| Dy$^{3+}$:PKBAFD10 | 1018 | 4.76                    | 0.58      | [42]       |
| Dy$^{3+}$:NbFSDy10 | 1489 | 6.13                    | 0.62      | [46]       |

For the emission color of Dy$^{3+}$-doped zinc phosphoborate glasses were characterized in the frame of the chromaticity color coordinates as follow equations [55]:

$$x = \frac{X}{X + Y + Z}; y = \frac{Y}{X + Y + Z}; z = \frac{Z}{X + Y + Z}$$

where $X$, $Y$ and $Z$ are the tritimulus values given by:

$$X = \int E(\lambda) \bar{x}(\lambda) d\lambda; \quad Y = \int E(\lambda) \bar{y}(\lambda) d\lambda; \quad Z = \int E(\lambda) \bar{z}(\lambda) d\lambda;$$

where $\bar{x}$, $\bar{y}$ and $\bar{z}$ are the matching functions of the Commisssion International de l’Eclairage (CIE). The CIE chromaticity color coordinates are shown in Figure 7 under exciting wavelength at 347 nm. The $(x, y)$ chromaticity color coordinates are found to be $(0.3892, 0.4362)$, $(0.3887, 0.4363)$, $(0.3894, 0.4364)$, $(0.3907, 0.4385)$ and $(0.3902, 0.4374)$ for ZPBD1, ZPBD2, ZPBD3, ZPBD4 and ZPBD5, respectively. These chromaticity coordinate values signified white emission color. Normally, white emission color appeared by the combination between yellow and blue emission of transition $^4F_{9/2} \rightarrow ^6H_{13/2}$ (573 nm) and $^4F_{9/2} \rightarrow ^6H_{15/2}$ (481 nm). Moreover, the Y/B ratio was corresponding to more sensitive with glass composition. The Y/B ratio of this work found to be 2.24, 2.29, 2.19, 2.19 and 2.18, respectively. Decreasing of Y/B ratio showed that the higher degree of covalence between Dy$^{3+}$ and oxygen/fluoride ions because of the increasing of electronegativity (EN) of the next neighbour element metal in the complex oxides Dy−O−M [50, 56].

The point on CIE chromaticity color coordinates point to Planckian radiation which indicated the quality of light source [57]. It well known as correlated color temperature (CCT). The CCT is calculated by McCamy approximate formula as follow equation [58]:

$$CCT = -449 n^3 + 352 n^2 - 6823.8 n + 5520.33,$$

where $n = (x - 0.3320)/(y - 0.1858)$, $x$ and $y$ are the chromaticity coordinates. The CCT for ZPBD1, ZPBD2, ZPBD3, ZPBD4 and ZPBD5 glasses were 3974 K, 3989 K, 3970 K, 3948 K and
3955 K, respectively. The CCT values of all glasses are found to be in warm white light region which are suitable for W-LEDs and solid state lighting materials [59].

**Figure 7.** The CIE chromaticity diagram showing the color coordinates of Dy\(^{3+}\)-doped zinc phosphoborate glasses for exciting wavelength at 347 nm.

### 4. Conclusions

The aim of this work was enhanced Dy\(^{3+}\)-doped zinc phosphoborate glass by substitution ZnO by ZnF\(_2\) for used to be W-LEDs and lighting materials. All glasses were prepared by melt quenching method and investigated though physical, optical absorption, photoluminescence, radiative properties and emission color. The densities of glasses were increased with the addition of ZnF\(_2\) replace ZnO because the molecular weight of ZnF\(_2\) is higher than ZnO. Also, the substitution of ZnO by ZnF\(_2\) was result of increasing of molar volumes since the fluoride ion created NBOs and F\(^-\) sites in glass which substitutes for BOs ions. The refractive indexes of Dy\(^{3+}\)-doped zinc phosphoborate glasses were increased since speed of light in glasses travel slowly. The absorption spectra exhibited eleven bands and were found to originate from a transition ground state \(^6\text{H}_{15/2}\) to excited state. The transition \(^6\text{H}_{15/2} \rightarrow ^4\text{P}_{7/2}\) showed the highest band in UV-visible range when compared to the other transition peaks that were observed. The absorbance of Dy\(^{3+}\)-doped zinc phosphoborate glasses was seen nearly. It indicated that the substitution of ZnO by ZnF\(_2\) is not effect to absorbance of glasses. The optical absorption spectra led to calculate JO parameters. The trend of JO parameters, the present glasses follow as \(\Omega_2 > \Omega_4 > \Omega_6\) indicated the similar site around Dy\(^{3+}\) ions, which may can be a basis for good host glasses for optical applications. The JO parameters along with emission spectra were used to predict radiation properties of Dy\(^{3+}\) ions in glass matrix. The emission spectra were found at wavelength at 481 nm, 573 nm, 662 nm and 752 nm under the excitation wavelength at 347 nm. When considering concentration of ZnF\(_2\) with the emission intensities, the emission intensity was seen to increase due to the reduction of OH groups. For radiative properties, the \(\beta_R\) values were higher than 50% which led to lasing power of a transition in glass matrix. While, the \(\sigma_{em}(\lambda)\) value of Dy\(^{3+}\)-doped zinc phosphoborate glasses increase when substituted ZnO by ZnF\(_2\). It showed that ZPBD5 were
suitable to utilize as lighting materials. The emission color of all glasses was characterized in the frame of the chromaticity color coordinates and investigated the CCT by McCamy approximate formula. The chromaticity coordinate values signified white emission color of all glasses whereas The CCT values of all glasses are found to be in warm white light region which are suitable for W-LEDs and solid state lighting materials.

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