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# **Research Article**

# IMPACT OF DYSPROSIUM CONCENTRATION ON LUMINESCENCE PROPERTIES OF ZINC PHOSPHATE GLASSES FOR PHOTONIC APPLICATIONS

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ARTICLE INFO	ABSTRACT	
Article History: Received 06 <sup>th</sup> August, 2015 Received in revised form 14 <sup>th</sup> September, 2016 Accented 23 <sup>rd</sup> October 2016	With interest in the luminescence properties, dysprosium doped six series of zinc phosphate glass composition with different concentrations (0.1, 0.3, 0.5, 1.0, 1.5 and 2.0 mol%) were prepared by melt quenching method, and their luminescence has been investigated. Structural properties were accomplished from XRD (X-Ray Diffractometer) and Raman spectrum. Spectroscopic properties were investigated by measuring optical absorption spectrum, excitation spectrum, emission spectra	

# Key Words:

Rare earth doped glasses; Judd-Ofelt theory; Emission properties; Absorption; Decay profiles; Dysprosium.

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melt quenching method, and their luminescence has been investigated. Structural properties were accomplished from XRD (X-Ray Diffractometer) and Raman spectrum. Spectroscopic properties were investigated by measuring optical absorption spectrum, excitation spectrum, emission spectra and decay profiles. Dysprosium environment in zinc phosphate host glass matrix can be accessed by Judd-Ofelt (J-O) theoretical approach. This theory gives three important parameters such as  $\Omega_2$ ,  $\Omega_4$ and  $\Omega_6$  parameters. In turn these parameters were further used to calculate emission properties of Dy<sup>3+</sup> ions. Luminescence parameters such as effective bandwidth ( $\Delta \lambda_{eff}$ ), stimulated emission crosssections ( $\sigma_p$ ) and branching ratios ( $\beta_{exp}$ ) have been studied through photoluminescence spectra. By adjusting the doping concentration in glass system, the concentration quenching phenomenons occur. The photoluminescence spectra exhibit three prominent transitions. Of which, the yellow transition has high emission intensity. Further, decay time constants have been estimated from the decay profiles of Dy<sup>3+</sup> doped different zinc phosphate glasses. This approach shows the present prepared zinc phosphate glasses significant for yellow lasing action.

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## **INTRODUCTION**

Among, the many different types of glasses and their derivatives, rare earth doped one has been investigated. In particular, oxide glasses possessing zinc have been used in solid state laser hosts, optical waveguides, phosphors, optical amplifiers and optical displays, due to thermal expansion coefficients. Addition of zinc into host glass matrix, it can be acts as a network former/modifier, so that it provides wide range of glass composition, low glass transition temperature and increases chemical durability [1,2]. According to these points of view, as well as the importance of finding efficient luminescent materials for the design of optical devices, oxy fluoride glasses got importance. In this investigation a spectroscopic analysis of the luminescence from the  $Dy^{3+}$  activated in zinc phosphate glass matrix is presented.

In order to achieve a better understanding of concentration quenching and energy transfer phenomenon, spectroscopic data for the  $Dy^{3+}$  doped zinc phosphate glasses are analyzed. Main advantages with dysprosium activators is, it gives high quantum efficiency associated with negligible multiphonon

relaxation because of the wide energy gap between the  ${}^{4}F_{9/2}$ emitting level and the next <sup>6</sup>F<sub>1/2</sub> level lying lower (7200 cm<sup>-1</sup>) [3]. The luminescence intensity particularly  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ yellow emission is a hypersensitive transition (forced electricdipole), such that it strongly depends on the ligand environment, whereas the  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$  blue emission is insensitive to ligand environment of host matrix. The yellowto-blue (Y/B) emission intensity ratio can vary significantly in great measure with host. If the Y/B ratio is larger than the unity, then the glasses can be suitable for laser light generation in the spectral region yellow. Moreover, the Y/B ratio is related with the  $\Omega_2$  Judd–Ofelt intensity parameter, so that a large value of  $\Omega_2$  leads to relatively high values of both the Y/B ratio and <sup>4</sup>F<sub>9/2</sub> level total emission probability [4]. High values of such parameters are required to achieve yellow laser oscillation at around 575 nm.

Trivalent dysprosium ions  $(Dy^{3+})$  doped glasses have been widely studied to obtain white light emission, by proper adjustment of yellow-to blue intensity ratio (Y/B) values because of its mainly consists of two fine bands in the blue (482 nm,  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ ) and yellow (575 nm,  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ )

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emissions.  $Dy^{3+}$  ion has large absorption cross-section [5]. In several hosts glasses doped with  $Dy^{3+}$  ion is known to give lasing transition in the NIR region at 1.35 and 3.0 mm. The lasing in visible region in glass hosts has important applications in commercial display optical sensors [6]. In recent years, the spectroscopic study of Dy<sup>3+</sup> ions in heavy metal lead-based glasses and glass-ceramics has been reported by Pisarska et al. [7]. Rajesh et al. [8] have investigated the structural and luminescence properties of strontium lithium bismuth borate glasses. The photoluminescence and energy transfer of Dy<sup>3+</sup> doped fluorophosphate glasses were studied by Praveena et al. [9]. Basavapoornima et al. [10] have investigated the luminescence and laser transition studies of Dy<sup>3+</sup> K-Mg-Al fluorophosphates glasses. Optical absorption and photoluminescence studies of  $Dy^{3+}$  doped alkaline earth bismuth borate glasses have been studied by Veeramohan Rao et al. [11]. The purpose of the present work is to prepare zinc phosphate (ZP) glass doped with Dy<sub>2</sub>O<sub>3</sub> and investigate their luminescence and lasing properties by absorption, photoluminescence and lifetimes for different applications in solid state lighting field.

The purpose of this study is to study zinc phosphate glasses doped with  $Dy^{3+}$  ions at a wide range of concentrations. The study includes material characterizations and analyses of structural, optical, photoluminescence, and decay lifetime characteristics with respect to the concentration variation of  $Dy^{3+}$  ions. Moreover, the effects of  $Dy_2O_3$  component on luminescence properties were studied. Finally, from the emission spectra of the glass samples were compared with literature and reported in this paper.

#### **Experimental techniques**

Different zinc phosphate (ZP) glasses were prepared by using raw materials (99.9%), ammonium phosphate ( $NH_4H_2PO_4$ ), lithium fluoride (LiF), strontium oxide (SrO), zinc oxide (ZnO) and dysprosium oxide ( $Dy_2O_3$ ). Final glass compositions of the prepared glass samples are labelled as follows (mol%):

1 Dy01	59.9NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> -10LiF-10SrO-20ZnO-0.1Dy <sub>2</sub> O <sub>3</sub>
2 Dy03	59.7NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> -10LiF-10SrO-20ZnO-0.3Dy <sub>2</sub> O <sub>3</sub>
3 Dy05	59.5NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> -10LiF-10SrO-20ZnO-0.5Dy <sub>2</sub> O <sub>3</sub>
4 Dy10	59.0NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> -10LiF-10SrO-20ZnO-1.0Dy <sub>2</sub> O <sub>3</sub>
5 Dy15	58.5NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> -10LiF-10SrO-20ZnO-1.5Dy <sub>2</sub> O <sub>3</sub>
6 Dy20	58.0NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> -10LiF-10SrO-20ZnO-2.0Dy <sub>2</sub> O <sub>3</sub>

Precise amounts of the starting materials in mol% were weighed out and grinded in an agate mortar to obtain homogeneous mixtures. The mixtures were placed in porcelain crucible and then heated in an electric furnace. After heating, the obtained liquid was poured on brass plate and then pressed by another brass plate. The obtained glasses were used for characterization.

Amorphous nature of the prepared glasses was verified by SEIFERT X-RAY diffractrometer. Raman spectrum has recorded JOBIN YVUON spectrometer. The optical absorption spectral measurements were collected using ELICO SL 218 double beam spectrophotometer in UV-VIS and NIR regions. The excitation, photoluminescence spectra and decay curves of  $Dy^{3+}$  doped glass samples were recorded using FLS-980 fluorescence spectrometer with xenon lamp as excitation source.

## **RESULTS AND DISCUSSION**

#### XRD analysis

The X-ray diffraction (XRD) profile for 0.5 mol% of  $Dy^{3+}$  doped ZP glass matrix is shown in Fig. 1. The analysis of the profiles shows no sharp diffraction peak, but a broad hump can be observed reflecting a characteristic of amorphous material. From this figure, it is apparent that no characteristic diffraction peaks, indicating that the prepared glass is amorphous in nature.



#### Raman spectrum

Fig.2 shows Raman spectrum of 0.5 mol% of  $Dy^{3+}$  doped ZP glass matrix. The low frequency band extended from 300-480 cm<sup>-1</sup> region is related to the bending motion of phosphate polyhedral PO<sub>4</sub> units with cations like ZnO and SrO etc. as the modifiers. The broad band at 773 cm<sup>-1</sup> is due to symmetric stretching of (P–O–P) bridging oxygen bonds in (P<sub>2</sub>O<sub>7</sub>)<sup>4</sup> units. [12-14]. This peak is a convolution of two peaks i.e. one may due to vibrations of the two joined Q<sup>2</sup> units and the second one to those of Q<sup>1</sup> units. Presence of last two bands indicates that due to addition of different modifiers into glass matrix, long range order of network become cut down and formed chain like units. This type of structural units increases glass strength.



#### Absorption spectrum and Judd-Ofelt theory

Absorption spectrum of 0.5 mol% of  $Dy^{3+}$  doped ZP glass sample in two regions of wavelength 350-510 nm (UV-VIS) and 700–1900 nm (NIR) are displayed in Fig. 3.



Fig.3 Absorption spectrum of 0.5 mol% of Dy<sup>3+</sup> doped zinc phosphate glass matrix

The observed thirteen absorption bands, which originated from the ground state  ${}^{6}H_{15/2}$  to higher states assigned to different transitions of  $Dy^{3+}$  ions by comparing the peak positions with reported literature [15]. The position of these absorption transitions of Dy05 zinc phosphate glass matrix located at 350, 363, 378, 387, 426, 452, 474, 751, 803, 897, 1091, 1276 and 1682 originates due to electric dipole (ED) transition from the  ${}^{6}H_{15/2}$  ground state to the various excited states of Dy<sup>3+</sup> such as  ${}^{6}P_{7/2}$ ,  ${}^{6}P_{3/2}$ ,  ${}^{4}M_{19/2}$ ,  ${}^{6}F_{7/2}$ ,  ${}^{4}G_{11/2}$ ,  ${}^{4}I_{15/2}$ ,  ${}^{4}F_{9/2}$ ,  ${}^{6}F_{3/2}$ ,  ${}^{6}F_{5/2}$ ,  ${}^{6}F_{7/2}$ ,  ${}^{6}F_{9/2}$ ,  ${}^{6}F_{11/2}$ + ${}^{6}H_{9/2}$  and  ${}^{6}H_{11/2}$ , respectively. The absorption band of Dy<sup>3+</sup> located at ~1276 nm corresponds to the hypersensitive transition dominated in intensity than other transitions of Dy<sup>3+</sup> ions. It is noted that, in the UV-VIS region, the absorption bands of different transition levels overlap each other and also week in intensities due to the presence of closed energy levels in Dy<sup>3+</sup> ions and this difficulties arises can be resolved by addition of both the dipole strengths and the squared reduced matrix elements of overlapping transitions.

**Table 1** Experimental  $(f_{exp})$  and calculated  $(f_{cal})$  spectral intensities  $(x10^{-6})$  of different absorption bands and Judd-Ofelt intensity parameters  $(\Omega_{\lambda}, x10^{-20} \text{ cm}^2)$  for Dy05 zinc phosphate glass matrix

Transition			
${}^{6}\text{H}_{15/2} \rightarrow$	$f_{exp}$	$\mathbf{f}_{cal}$	
<sup>6</sup> H <sub>11/2</sub>	2.91	3.06	
${}^{6}F_{11/2} + {}^{6}H_{9/2}$	15.17	16.32	
<sup>6</sup> F <sub>9/2</sub>	5.42	5.42	
<sup>6</sup> F <sub>7/2</sub>	4.87	4.83	
<sup>6</sup> F <sub>5/2</sub>	2.72	2.58	
${}^{6}F_{3/2}$	0.38	0.44	
${}^{4}F_{9/2}$	0.20	0.37	
<sup>4</sup> I <sub>15/2</sub>	0.99	1.08	
${}^{4}G_{11/2}$	0.40	0.14	
${}^{4}F_{7/2}$	1.17	1.45	
${}^{4}M_{19/2}$	0.18	1.49	
${}^{6}P_{5/2} + {}^{6}P_{3/2}$	2.02	2.11	
${}^{6}\mathrm{P}_{7/2}$	4.17	3.91	
$\delta_{rms}$	±0.	±0.51	
$\Omega_2$	4.67		
$\Omega_4$	2.01		
$\Omega_6$	0.98		

The corresponding reduced matrix elements have been also added. In the case of NIR region, the absorption bands have stronger intensities. Therefore the absorption bands mainly due to transition present in the NIR region impact on J-O parameters.

The Judd–Ofelt (JO) theory [16, 17] is used to characterize radiative transitions for  $Dy^{3+}$  doped glasses. It gives three set of intensity parameters,  $\Omega_{\lambda}$  ( $\lambda$ =2, 4 and 6), that are sensitive to the around the environment of the dysprosium ions. The experimental oscillator strengths,  $f_{exp}$ , of the absorption bands can be calculated by

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

where  $\varepsilon(v)$  is the molar extinction coefficient. According to the Judd-Ofelt theory (J- O), the spectral intensity of an electric dipole absorption transition can be defined from the initial state, aJ to the final state, bJ'.

$$f_{cal}(aJ, bJ') = \frac{8\pi^2 mc \nu}{3hc^2(2J+1)} \left[ \frac{(n^2+2)^2}{9n} \right] \sum_{\lambda=2,4,6} \Omega_{\lambda} |< aJ || U^{\lambda} || bJ' >|^2$$

In the above equation, all symbols are as usual meaning. The Judd-Ofelt intensity parameters  $\Omega_{\lambda}$  are obtained from the experimental absorption band. The root mean square (RMS) deviation value of  $0.51 \times 10^6$  is obtained between the experimental and calculated oscillator strengths, indicates that good fit between two magnitudes and also good consistency of J-O intensity parameters. These results are shown in Table 2. It is observed that order of  $\Omega_{\lambda}$  parameters is  $\Omega_2 > \Omega_4 > \Omega_6$  for the Dy05 glass matrix.

**Table 2** Radiative transition probabilities  $(A_R)$  (s<sup>-1</sup>), total transition probabilities  $(A_T)$ , branching ratios  $(\beta_R)$ , and radiative lifetimes  $(\tau_R)$  (µs) of certain excited levels for Dy05 zinc phosphate glass matrix

SLJ	S'L'J'	$A_R$	$\beta_R$	
${}^4F_{9/2} \rightarrow$	<sup>6</sup> F <sub>3/2</sub>	0	0	
	<sup>6</sup> F <sub>5/2</sub>	6	1	
	6F7/2+6H5/2	2	0	4 711
	6F9/2+6H7/2	20	2	$A_T = /11$
	6F11/2+6H9/2	29	4	$t_{\rm R} = 1400$
	<sup>6</sup> H <sub>11/2</sub>	52	7	
	<sup>6</sup> H <sub>13/2</sub>	497	70	
	<sup>6</sup> H <sub>15/2</sub>	105	15	

High  $\Omega_2$  parameter and low  $\Omega_6$  parameter related to covalency and rigidity respectively is observed.

J-O intensity parameters are further used to evaluate the different radiative properties like radiative transition probability (A<sub>R</sub>), radiative lifetime ( $\tau_R$ ) and branching ratios ( $\beta_R$ ), of certain excited states are calculated for Dy05 glass matrix and are collected in Table 2 for  ${}^6F_{9/2}$  state of Dy<sup>3+</sup>.

The radiative lifetimes  $(\tau_R)$  and branching ratios  $(\beta_R)$  can be calculated using the equations

$$\tau_{rad} = \frac{1}{\sum_{bJ} A_{rad} (aJ, bJ')^{-1}}$$
$$\beta_{R} (aJ, bJ') = \frac{A_{rad} (aJ, bJ')}{\sum_{bJ'} A_{rad} (aJ, bJ')}$$

It is noticed (from Table 2) that the  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ ,  ${}^{6}H_{13/2}$  and  ${}^{6}H_{11/2}$  transitions have  $A_R$  magnitude greater than >50 s<sup>-1</sup> and more branching ratios.

#### Fluorescence properties

The excitation spectrum for Dy05 ZP glass matrix is recorded by choosing emission wavelength as 574 nm and is shown in Fig. 4. From the excitation spectrum, seven prominent bands were observed at 324, 350, 365, 387, 425, 452 and 472 nm ascertained from  ${}^{6}H_{15/2}$  to  ${}^{4}K_{15/2}$ ,  ${}^{6}P_{7/2}$ ,  ${}^{4}I_{13/2} + {}^{4}F_{7/2}$ ,  ${}^{4}G_{11/2}$ ,  ${}^{4}I_{15/2}$  and  ${}^{4}F_{9/2}$  transitions, respectively.



Fig.4 Excitation spectrum of 0.5 mol% of Dy3+ doped zinc phosphate glass matrix

The transition  ${}^{6}H_{15/2}$  to  ${}^{4}I_{13/2} + {}^{4}F_{7/2}$  observed at 387 nm is more intense and selected as excitation source. Fig. 5, shows the luminescence emission spectra for Dy01, Dy03, Dy05, Dy10, Dy15 and Dy20 glasses in the range of wavelength 430–700 nm under the excitation wavelength of 387 nm. In the present study, three emission peaks are observed at 484, 574 and 663 nm corresponding to  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ ,  ${}^{6}H_{13/2}$  and  ${}^{6}H_{11/2}$  transitions, respectively. From the emission spectra it is clearly observed that emission intensities increases upto 0.5 mol% of dysprosium and then decreases with the increase of Dy<sup>3+</sup> concentration. This is due to concentration quenching. It is occur due to the increasing of non-radiative (NR) energy transfer through cross relaxation and resonant energy channels among Dy<sup>3+</sup> ions [18].



**Fig.5** Emission spectra of different concentrations of Dy<sup>3+</sup> doped zinc phosphate glasses

From Fig.5, the most intense emission is observed for the  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$  yellow transition than the  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$  blue emission transition. The intensity of the  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$  yellow emissions is a hypersensitive (forced electric-dipole) transition, and it exhibits a strong dependence on the ligand environment, whereas the intensity of the  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$  blue emission is insensitive to the host. Thus, the yellow-to-blue (Y/B) emission intensity ratio can differ in different hosts. The glass can be said advantageous for better light emission either yellow or blue depends on the Y/B ratio magnitude, whether larger or less than the unity. In the present work, Y/B ratio magnitudes were found to be 2.97, 2.99, 3.13, 3.01, 2.98 and 2.95 for Dy01, Dy05, Dy10, Dy15 and Dy20 glasses respectively. This magnitude signifies that Y/B ratio increases initially upto 0.5 mol% and then decreases with increase in Dy<sup>3+</sup> concentration level. Among different ZP glasses, Dy05 (3.13) has higher and Dy20 (2.95) has lower Y/B ratios. The prepared ZP glass possesses Y/B ratios greater than unity and hence this ZP glass host can be useful for yellow light emission.

From the emission spectra, the intensity of probable lasing transition can be assessed, like branching ratio ( $\beta_{exp}$ ), from area under the emission band, the effective line widths ( $\lambda_{eff}$ ) and peak stimulated emission cross-sections ( $\sigma_P$ ) for the certain transitions,  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{I}$  (J =15/2, 13/2, 11/2 and 9/2).

The peak stimulated emission cross-section ( $\sigma_P$ )

$$\sigma_{\rm p}({\rm aJ, bJ'}) = \frac{\lambda_{\rm p}^4}{8\pi {\rm cn}^2 \Delta \lambda_{\rm eff}} A_{\rm rad}({\rm aJ, bJ'})$$

where  $\lambda_P$  is emission peak wavelength and  $\Delta \lambda_{eff}$ , is the effective linewidth.

The higher  $\sigma_P$  is very important property for low threshold and high gain laser application [19]. From the three emission transitions of  $Dy^{3+}$  ion,  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$  transition has higher  $\sigma_P$ than rest of transitions and among all concentrations of  $Dy^{3+}$ , Dy05 zinc phosphate glass matrix shows higher  $\sigma_P$  i.e.  $45.74x10^{-22}cm^{2}$ . The value of  $\sigma_P$  for the  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$  yellow transition of the Dy05 glass is found to be high. Hence, the glass Dy05 glass matrix might be useful for yellow lasing material through  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$  transition. The  $\beta$  is one of the important and attractive parameter to determine lasing power of a particular transition and it is well established that an emission transition having the values of  $\beta$  is greater than 50% is can be considered as more as potential for laser emission. The experimental branching ratio ( $\beta_{exp}$ ) are measured under the relative areas of the each individual emission transitions. In the present study it is observed that there is a good agreement between  $\beta_{exp}$  and  $\beta_R$ .

#### **Decay kinetics**

With 387 nm excitation, into the  ${}^{6}H_{15/2} \rightarrow {}^{4}I_{13/2}$  absorption (excitation) band and then the  ${}^{4}I_{13/2} \rightarrow {}^{4}F_{9/2}$  transition is more favourable way to depopulate nonradiatively through the multiphonon relaxation (MPR) due to the fact that the energy gap between them is low. No emissions from other energy levels are expected. The MPR from the  ${}^{4}F_{9/2}$  level is negligible owing to fact that the next level ( ${}^{6}F_{1/2}$ ) lies lower by about ~6900 cm<sup>-1</sup>. This wide energy gap between the  ${}^{4}F_{9/2} \leftrightarrow {}^{6}F_{1/2}$  levels leads to a high quantum efficiency of the  ${}^{4}F_{9/2}$  emitting level.

The fluorescence decay profiles for  ${}^{4}F_{9/2}$  level of  $Dy^{3+}$  doped zinc phosphate glasses with the variation of  $Dy^{3+}$  content while maintaining with a fixed emission at 574 nm, which corresponds to the electronic transition  $({}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2})$  and excitation at 387 nm is displayed in Fig. 6. Fluorescence lifetimes were measured form e-folding time of the emission intensities. For the decay curves which are bi-exponential behavior, the resultant decay lifetime can be calculated using the formula [5]



Fig.6 Decay profiles for different concentrations of Dy<sup>3+</sup> doped zinc phosphate glasses

$$I(t) = A_1 \exp(\frac{-t}{\tau_1}) + A_2 \exp(\frac{-t}{\tau_2})$$

where 'I' is the photoluminescence intensity at any time 't' after switching off the excitation illumination,  $\tau_1$  and  $\tau_2$  are fast and slow decay times respectively, A<sub>1</sub>, A<sub>2</sub> are respective fitting (weighing) parameters. The first term in the equation refers to excited state absorption and second term refers to the energy transfer (ET) process or in other words radiative and non-radiative decays.

The experimental lifetimes  $(\tau_{\text{exp}})$  have been evaluated using the relation

$$\tau_{\rm exp} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

<b>Table 3</b> Emission band positions ( $\lambda_p$ , nm), effective
bandwidths ( $\Delta\lambda_{eff}$ , nm) transition probabilities (A) (s <sup>-1</sup> ),
peak stimulated emission cross-sections ( $\sigma_{p_1} \times 10^{-22} \text{ cm}^2$ ) and
experimental branching ratios ( $\beta_{exp}$ , %), and calculated
branching ratios ( $\beta_{exp}$ , %) of ${}^{4}F_{9/2}$ state of Dy05 zinc
nhosphate glass matrix

Transition	$\lambda_{\mathrm{p}}$	$\Delta \lambda_{eff}$	Α	σΡ	β <sub>exp</sub>	β <sub>cal</sub>
${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$	484	17	105	3.57	18	15
<sup>6</sup> H <sub>13/2</sub>	574	15	497	45.74	69	70
${}^{6}\text{H}_{11/2}$	663	16	52	1.35	13	7

It is observed that the decay lifetimes decreases with increasing dysprosium content in the ZP glass system. The lifetimes were found to be 0.85, 0.83, 0.80, 0.72, 0.65 and 0.52 ms for the Dy01, Dy03, Dy05, Dy10, Dy15 and Dy20 ZP glasses respectively. The decay lifetime decreases from 0.83 ms to 0.52 ms. This gradual decrease in lifetime is consistent with the steady state luminescence behavior which is due to the increase in non-radiative transition processes to excited states of Dy<sup>3+</sup> ions (Fig. 6). However, the lifetime value drops to 0.52 ms when  $Dy^{3+}$  content increases to 2.0 mol% which might be due to the larger amount of activator ions in the glass system. Except Dy01, Dy03 and Dy05 glasses, all ZP glasses of decay profiles are fitted non-exponential function at short times. This type of activity is due to energy transfer (ET) between two Dy<sup>3+</sup> atoms and concentration quenching. In order to investigate the process involved in the ET mechanism, the nonexponential decay curves for the  ${}^{4}F_{9/2}$  level of Dy<sup>3+</sup> ions have been analyzed using Inokuti–Hirayama (I-H) model [9-11].

 $I(t)=I_0\exp\{-t/\tau_0-Q(t/\tau_0)^{3/S}\}$ 

where t is the time,  $\tau_0$  is the intrinsic decay time of donors in the absence of acceptors, energy transfer parameter (Q). The Q value linked to variable interaction parameter, S and the gamma function  $\Gamma(x)$  parameters.  $\sqrt{\Pi}$  is 1.77 (for S=6, dipole– dipole), 1.43 (for S=8, dipole–quadrupole) and 1.33 (for S=10, quadrupole–quadrupole). In co-doped system, decays were fitted to S=6. From this model it is assessed that ET occurs through dipole–dipole (d-d) interaction.

### **CONCLUSIONS**

In the present study, dysprosium doped six series of zinc phosphate glass composition with different concentrations (0.1,0.3, 0.5, 1.0, 1.5 and 2.0 mol%) were prepared by melt quenching method, and their luminescence has been investigated. Structural properties were accomplished from (X-Ray Diffractometer) and Raman spectrum. XRD Spectroscopic properties were investigated by measuring optical absorption spectrum, excitation spectrum, emission spectra and decay profiles. Dysprosium environment in zinc phosphate host glass matrix can be accessed by Judd-Ofelt (J-O) theoretical approach. It is observed that order of  $\Omega_{\lambda}$ parameters is  $\Omega_2 > \Omega_4 > \Omega_6$  for the zinc phosphate glasses. High  $\Omega_2$  parameter and low  $\Omega_6$  parameter related to covalency and rigidity respectively is observed. J-O intensity parameters are used to further to evaluate the different radiative properties like radiative transition probability (A<sub>R</sub>), radiative lifetime ( $\tau_R$ ), branching ratios ( $\beta$ ), of certain excited states. It is noticed that  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ ,  ${}^{6}H_{13/2}$  and  ${}^{6}H_{11/2}$  transitions have  $A_{R}$  magnitude greater than  $>50 \text{ s}^{-1}$  and more branching ratios. Luminescence parameters such as effective bandwidth ( $\Delta \lambda_{eff}$ ), stimulated emission cross-sections ( $\sigma_n$ ) and branching ratios ( $\beta_{exp}$ ) have been studied through photoluminescence spectra. By adjusting the doping concentration in glass system, the quenching was observed in emission intensity. The photoluminescence spectra exhibit three prominent transitions. Of which, the yellow transition has high emission intensity. Furthermore it is also noticed that the present glass (Dy05) sample shows higher emission cross-section for  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$  transition. The value of  $\sigma_P$  for the  ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$  yellow transition of the Dy05 glass is found to be high. Hence, the glass Dy05 for  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ transition might be useful for yellow lasing material. Further, decay time constants have been estimated from the decay profiles of Dy<sup>3+</sup> doped different zinc phosphate glasses. It is observed that the decay lifetimes decreases with increasing dysprosium content in the ZP glass system. PL decay lifetimes are determined by fitting the decay data with the mono exponential decay equation. The decay lifetimes decreases with increasing of Dy<sup>3+</sup> concentration. This gradual decrease in lifetime is consistent with the steady state luminescence behavior which is due to the increase in non-radiative transition processes to excited states of Dy3+ ions. This approach shows the present prepared zinc phosphate glasses useful towards the development of yellow lasing materials.

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