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Optical Properties of Dy^{3+} Doped Zinc Boro-Phosphate Glasses for Photonic Applications

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Abstract

Zinc boro-phosphate glasses doped with Dy^{3+} ions (DZBP) have been synthesized following the melt quenching technique and their spectroscopic properties were studied through absorption and emission spectra. The bonding parameters (δ and β) and Judd-Ofelt (JO) intensity parameters were calculated from the absorption spectra. The luminescence properties of the present Dy^{3+} doped glasses have been analyzed through radiative properties. The luminescence spectra of the Dy^{3+} doped zinc boro-phosphate glasses exhibit two intense emission bands corresponding to the $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transitions. The Y/B intensity ratio values have been calculated from the emission spectra of the prepared glasses and the combination of dominant blue and yellow emissions generate white light emission. The results obtained from the CIE chromaticity diagram suggest that the present Dy^{3+} doped glasses are suitable for white light applications.

Keywords: Absorption Spectra, Bonding Parameter, JO intensity parameter, luminescence, radiative properties.

1. Introduction

Nowadays, many researchers focus on rare earth (RE) ions doped optical materials for solid state lighting (SSL) applications such as white LEDs, color displays and cellular phone illumination etc., [1,2]. Among the several rare earth ions, Dy^{3+} ions play a vital role in the design and development of white LED's because of the dominant two emission bands in the visible region corresponding to the $^4F_{9/2}\rightarrow{}^6H_{15/2}$ (blue), $^4F_{9/2}\rightarrow{}^6H_{13/2}$ (yellow) transitions [3]. The Y/B intensity ratio depends upon structural changes in the environment around the Dy^{3+} ions and the white light emission has been obtained by adjusting the Y/B ratio by optimizing the RE ions concentration, chemical composition, pumping wavelength and heat treatment. B. Shanmugavelu et al. [4] and K. Swapna et al. [5] have also studied the variation of Y/B ratio for the white light applications. In the present work, Emission properties of Dy^{3+} doped zinc boro-phosphate glasses have been analyzed for the fabrication of white light emitting devices and the results are discussed and reported.

2. Experimental

The Dy^{3+} doped Zinc boro-phosphate glasses with the chemical composition $(59–x)P_2O_5+ xB_2O_3 + 10SrO + 10BaF_2 + 20ZnO + 1Dy_2O_3$ (where x = 10, 20, 30 and 40 in wt %) have been prepared by conventional melt quenching technique [6] and labeled as 10DZBP, 20DZBP, 30DZBP and 40DZBP based on the borate content. The absorption spectra were recorded between 400 and 2000 nm using Perkin-Elmer-Lambda 950 UV/Vis/NIR spectrophotometer with a resolution of ±0.1 nm. Luminescence spectra of the glasses were measured employing Perkin Elmer LS55 spectrophotometer in the wavelength range 450–700 nm with a spectral resolution of ±1.0 nm. All these measurements were carried out at room temperature (RT) only.

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3. Absorption Spectra and Bonding Parameter

The optical absorption spectra of the prepared Dy^{3+} doped Zinc boro-phosphate glasses recorded in the visible and near infrared regions are shown in figure 1. The absorption spectra exhibit eight inhomogeneous bands at around 1680, 1273, 1092, 900, 800, 750, 471 and 451 nm due to the absorption transitions from the $^6H_{15/2}$ ground state to the various excited states such as $^6H_{11/2}$, $^6F_{11/2}+^6H_{9/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}+^6H_{5/2}$ and $^4I_{15/2}$. From the absorption spectra, it is observed that the $^6H_{15/2} \rightarrow {}^6F_{11/2}+{}^6H_{9/2}$ transition is sensitive to the ligand environment around the RE ion site which obey the selection rules $|\Delta S| = 0, |\Delta L| \leq 2$ and $|\Delta J| \leq 2$ and is known as hypersensitive transition.

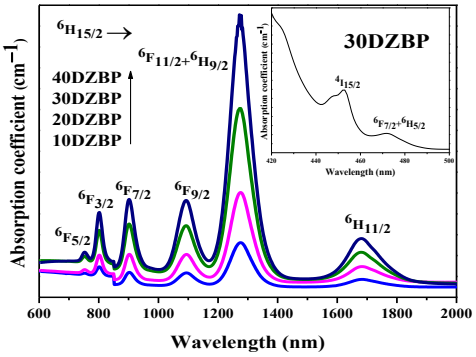

Figure 1. NIR absorption spectra of the Dy^{3+} doped zinc boro-phosphate glasses [Inset shows the absorption spectrum of the 30DZBP glass in the visible region]

From the optical absorption spectra, Nephelauxetic ratios and bonding parameter values have been calculated using the expressions reported in the literature [6] to study the nature of the Dy^{3+}-ligand bond in the prepared glasses and the values are presented in table 1. The positive sign of the δ values indicate the fact that the Dy–O bond is of covalent in nature and the covalency increases due to the increase in the B_2O_3 content in the studied glasses.

4. Judd-Ofelt Intensity Parameters

The JO intensity parameters (Ω_2, Ω_4 and Ω_6) provide information about the local structure of the ligand environment and nature of the metal-ligand bonds in RE doped glasses and the values are shown in table 1. It is observed from the table that the magnitude of the JO intensity parameters follow the trend as $\Omega_2>\Omega_6>\Omega_4$ uniformly for all the studied glasses and the Ω_2 values were found to increase with the increase in borate content in the prepared glasses compared to the reported literature [7,8] thus indicates the increasing asymmetry in the prepared glasses. Spectroscopic quality factor is ($\chi=\Omega_4/\Omega_6$) used to predict the stimulated emission in any active medium and is found to be higher for 30DZBP glass compared to other prepared glasses thus suggests its suitability for the photonic applications.

Table 1. Judd-Ofelt ($\times 10^{-20}$cm^2) parameters and bonding parameters ($\bar{\beta}$ and δ) of the Dy^{3+} doped zinc boro-phosphate glasses

Glass code	JO Parameters			Ω_4/Ω_6	$\bar{\beta}$	δ
	Ω_2	Ω_4	Ω_6			
10 DZBP	5.24	1.72	2.60	0.66	0.989	0.993
20 DZBP	7.13	1.20	1.54	0.77	0.990	1.006
30 DZBP	8.47	1.71	1.95	0.87	0.990	1.019
40 DZBP	8.51	1.73	3.75	0.46	0.991	1.023
LKZBSB[7]	5.36	1.46	1.95	0.74	-	-
BaO–TeO_2[8]	3.20	1.35	2.47	0.54	-	-

5. Luminescence spectral analysis

Figure 2 shows the luminescence spectra of the prepared Dy^{3+} doped zinc boro-phosphate glasses monitoring an excitation wavelength at 387 nm.

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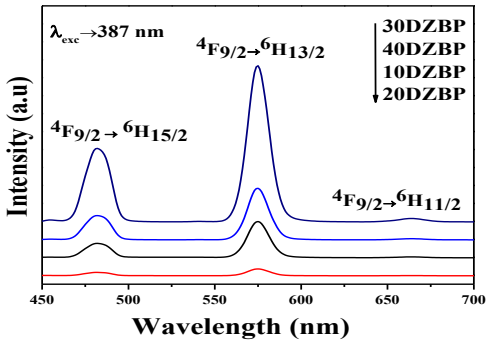

Figure 2. Emission spectra of the Dy^{3+} doped zinc boro-phosphate glasses

The luminescence spectra exhibit three emission bands centered at 482, 575 and 664 nm attributed to the $^4F_{9/2}\rightarrow{}^6H_{15/2}$ (blue), $^4F_{9/2}\rightarrow{}^6H_{13/2}$ (yellow) and $^4F_{9/2}\rightarrow{}^6H_{11/2}$ (red) transitions respectively. Among these transitions, $^4F_{9/2}\rightarrow{}^6H_{13/2}$ possess higher intensity compared to the other transitions and the ratio between integral intensities of $^4F_{9/2}\rightarrow{}^6H_{13/2}$ (yellow) and $^4F_{9/2}\rightarrow{}^6H_{15/2}$ (blue) transitions helps one to determine the local symmetry around the Dy^{3+} ion site. These values are found to increase with the increase in borate content in the prepared glasses indicating the increasing asymmetry in the prepared glasses. The luminescence intensity increases with the increase in borate content and found to quench beyond 30 wt% of B_2O_3 content in the prepared glasses.

6. Radiative properties

The radiative properties of the Dy^{3+} doped zinc boro-phosphate glasses have been calculated from the emission spectra using JO theory and the results are shown in table 2.

Table 2. Emission band position (λ_p, nm stimulated emission cross-section ($\sigma_P^E \times 10^{-22}$ cm^2), experimental and calculated branching ratios (β_R) values and Y/B intensity ratio values and (x, y) co-ordinates of the Dy^{3+} doped zinc boro-phosphate glasses

Transition parameters		10DZ BP	20DZ BP	30DZ BP	40DZ BP
$^4F_{9/2}\rightarrow{}^6H_{15/2}$	λ_p	482	482	482	481
	σ_P^E	1.2999	2.6911	3.4920	3.4284
	β_R(Exp)	0.2295	0.2977	0.2287	0.2910
	β_R(Cal)	0.4537	0.4474	0.4689	0.4318
$^4F_{9/2}\rightarrow{}^6H_{13/2}$	λ_p	574	574	584	574
	σ_P^E	46.5589	27.8518	63.3970	59.1955
	β_R(Exp)	0.7638	0.7088	0.7700	0.7399
	β_R(Cal)	0.6408	0.6583	0.6934	0.6864
$^4F_{9/2}\rightarrow{}^6H_{11/2}$	λ_p	663	664	674	663
	σ_P^E	7.1590	6.7055	9.8339	8.1244
	β_R(Exp)	0.0908	0.0774	0.0703	0.0797
	β_R(Cal)	0.0862	0.0919	0.0931	0.0918
x		0.372	0.371	0.381	0.375
y		0.379	0.368	0.379	0.373
Y/B intensity ratio		1.529	1.607	1.608	1.767

The branching ratio values of the $^4F_{9/2}\rightarrow{}^6H_{13/2}$ emission transition is found to be higher compared to the other emission transitions and follow the trend as $^4F_{9/2}\rightarrow{}^6H_{13/2} > {}^4F_{9/2}\rightarrow{}^6H_{15/2} > {}^4F_{9/2}\rightarrow{}^6H_{11/2}$ uniformly for all the prepared glasses. Among all the observed transitions, the σ_P^E value is found to be higher for the $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition pertaining to the prepared 30DZBP glass and further it possess higher σ_P^E value compared to the reported glasses PTBDy10 (2.86×10^{-21}cm^2) [9], Dy^{3+}: NMAP (25.65×10^{-22}cm^2) [10] thus suggests its suitability for yellow laser applications.

7. White Light Stimulation

Figure 3 shows the CIE diagram plotted for the prepared Dy^{3+} doped zinc boro-phosphate glasses using the expressions reported in the literature [6]. The x, y coordinate values are presented in table 2

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and are found to be closer to the standard equal energy point thus confirms the suitability of the present glasses for white light applications. In general, cool white light sources (high CCT values) are mostly used in schools, houses, hospitals etc.,

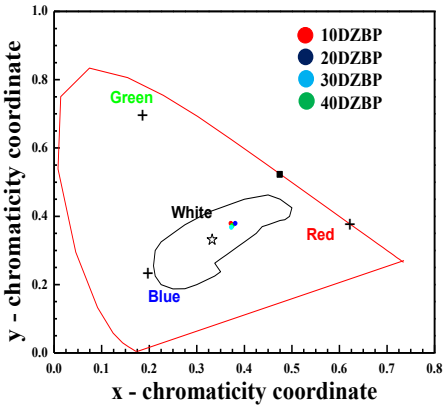

Figure 3. The CIE 1931 color chromaticity diagram of the Dy^{3+} doped zinc boro-phosphate glasses

The warmer white light sources (low CCT values) are used in offices, restaurants, hotels etc., The calculated CCT values for the prepared glasses are found to be 3641K, 4131K, 6234K and 3510K corresponds to the 10DZBP, 20DZBP, 30DZBP and 40DZBP glasses respectively. Among them, 30DZBP glass possesses higher CCT value suggesting its suitability for cool white light applications.

8. Conclusion

The covalency nature of the Dy–O bond increases with the increase in borate content in the prepared glasses. The Ω_2 and Y/B ratio values increases with the increase in borate content thus indicates the increasing asymmetry in the prepared glasses. Higher stimulated emission cross-section and branching ratio values of the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition corresponding to the 30DZBP glass confirms its suitability for yellow laser applications. The CIE color chromaticity coordinates (x, y) and higher CCT values suggests that the 30DZBP glass is a better choice for cool white light applications.

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