Absorption and Emission Analysis of Dy^{3+} Doped Fluoroborate Glasses for White Light Application

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Abstract. The Dy^{3+}-doped fluoroborate glasses with the composition (40-x)B_2O_3+20ZnO+20$MgCO_3$+20NaF+xDy_2O_3 (where x= 0.1, 0.3 and 1.0) have been prepared by conventional melt quenching technique. The bonding parameter and oscillator strength for the prepared glasses have been calculated using the optical absorption spectra. Judd–Ofelt (JO) intensity parameters (Ω_λ, λ = 2,4,6) have also been evaluated using optical absorption spectra. The radiative properties such as radiative transition probabilities (A), stimulated emission cross-section(σ_P^E), lifetime (τ_R) and branching ratios (β_R) have been calculated from luminescence spectra corresponding to $^4F_{9/2}\rightarrow{}^6H_{13/2}$ and $^6H_{15/2}$ of excited levels of Dy^{3+} ion. The CIE chromaticity color coordinates were evaluated from the emission spectra for all the glasses and found that they fall in the white light region. The dependence of spectral characteristic of Dy^{3+} ions due to concentration changes have been investigated and reported. The study concludes that the Dy^{3+} doped fluoroborate glasses are attractive material for white light applications.

INTRODUCTION

The rare-earth ions in crystals as well as glasses impart new potential of practical applications for their noticeable optical properties and high luminescence efficiency. Rare Earth (RE) ions provide an excellent active luminescent center due to their characteristic 4f-4f or 5d-4f emission transitions. Rare earth doped glass material is of significant importance owing to their potential applications in the fields of optoelectronic devices, laser, solid state lighting (SSL), biomedical, sensors and fiber optic amplifiers etc., [1,2]. Several glassy materials such as borates, phosphates, tellurites, fluorides, fluorophosphates and fluroborates have been widely investigated to understand the effect of host glass on the lasing properties of rare earth ions. Among the various glass formers, Borate (B_2O_3) is considered to be a good glass former on its own because of its low melting point, high transparency, good rare earth ions solubility and higher phonon energy. In the case of addition of sodium fluoride (NaF) in the borate glass, it reduces the phonon energy [2]. Among the different rare earth ions, Dy^{3+} is one of the important rare-earth ions with an attractive laser. The important task to generation white light from Dy^{3+} doped glasses at suitable yellow to blue (Y/B) intensity ratio can be achieved by varying the composition of the glass and excitation wavelengths. The Dy^{3+} ions are usually doped with the luminescent materials for the generation of white light in glasses. The present work reports optical analysis of Dy^{3+}-doped fluoroborate glasses for White LED's Application.

EXPERIMENTAL TECHNIQUE

The Dy^{3+} doped fluoroborate glasses were prepared by the conventional melt quenching technique [1]. H_3BO_3, ZnO, $MgCO_3$, NaF and Dy_2O_3 chemicals were used for the preparation of glasses and purchased from Sigma Aldrich with purity grade of 99.99%. The optical absorption spectra of all the prepared glasses were measured in the spectral region 350–1900 nm by JASCO V-670 UV–Vis–NIR spectrophotometer. The luminescence spectra were recorded in the LS 45 Perkin-Elmer paragon spectrometer.

RESULTS AND DISCUSSION

Optical Absorption Studies and Bonding Parameter

The Optical absorption spectra of the Dy^{3+} doped fluoroborate glasses recorded in the wavelength region 350−1900 nm are shown in **FIGURE 1**. The absorption spectra exhibit several in-homogeneously broadened bands due to f–f transitions from the ground state $^6H_{15/2}$ to various excited state in the prepared glasses. Among the absorption transitions for the present work, $^6H_{15/2}\rightarrow{}^6F_{11/2}$ transition is found to be hypersensitive in nature indicating that it is highly sensitive to the environment around the RE ion. It must be obeying some selection rules such as $\Delta S=0$, $|\Delta L|\leq 2$ and $|\Delta J|\leq 2$ [3]. The covalent or ionic in nature of the prepared glasses have been confirmed from the idea of Dy^{3+} ligand bond. The metal ligand bond can be covalent or ionic depending upon the positive or negative sign of δ. The bonding parameters are presented in **TABLE 1** as –1.3594 (BZMD0.1), –1.0697 (BZMD0.3) and 0.9857 (BZMD1.0). This values confirm that the Dy-O bond in Dy^{3+}:BZMDx glasses exhibits its tendency towards ionic nature.

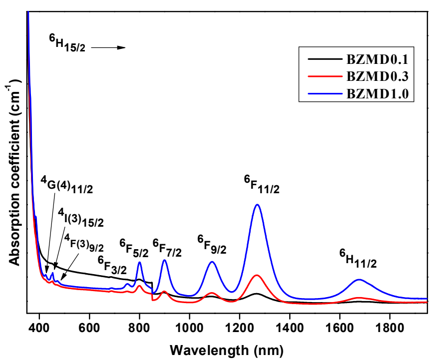

FIGURE 1. Optical Absorption spectra of the Dy^{3+} doped fluoroborate glasses

TABLE 1. Experimental and calculated oscillator strengths ($\times10^{-6}$) and JO parameters (Ω_λ, 10^{-20} cm^2) of the Dy^{3+} doped fluoroborate glasses

Transition	**BZMD0.1**		**BZMD0.3**		**BZMD1.0**	
$^6H_{15/2}\rightarrow$	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}
$^4G_{11/2}$	-	-	0.781	0.090	0.250	0.030
$^4I_{15/2}$	-	-	1.736	0.388	0.668	0.554
$^4F_{9/2}$	1.927	0.123	0.899	0.149	0.288	0.194
$^6F_{3/2}$	1.087	0.149	0.497	0.163	0.242	0.243
$^6F_{5/2}$	1.537	0.790	1.418	0.864	1.609	1.293
$^6F_{7/2}$	1.974	1.582	2.141	1.959	2.116	2.481
$^6F_{9/2}$	1.533	1.666	2.525	2.597	2.393	2.314
$^6F_{11/2}$	4.313	4.261	6.398	6.366	6.450	6.460
$^6H_{11/2}$	0.567	0.973	0.881	1.151	1.651	1.573
N	7		9		9	
σ_{rms}	±0.848		±0.614		±0.187	
$\overline{\beta}$	1.0137		1.0108		1.0099	
δ	–1.3594		–1.0697		–0.9857	
Ω_2	4.763		6.236		7.699	
Ω_4	2.768		2.489		6.443	
Ω_6	1.893		2.069		3.057	
Ω_4/Ω_6	1.462		1.203		2.107	
(Y/B)	1.212		1.194		1.201	

Oscillator Strength and J-O Intensity Parameter

The experimental oscillator strength (f_{exp}) of the absorption bands are calculated from the relative areas under the absorption bands of the individual transition in the absorption spectra of the RE ions doped materials. The J-O theory [4,5] has been applied to evaluate the intensity parameters Ω_λ (λ = 2, 4, 6) from the measured spectral intensities of absorption bands. The experimental and calculated oscillator strength ($\times10^{-6}$) of the Dy^{3+} doped fluoroborate glasses with rms (σ) deviation values are presented in **TABLE 1**. The JO analysis for the Dy^{3+} ions is in good agreement with (f_{exp}) and (f_{cal}) for some of the energy levels and there is an amount of moderate deviation in case of weak transition. The obtained J-O intensity parameters are as follows Ω_2=7.699 × 10^{-20}cm^2, Ω_4=6.443 × 10^{-20}cm^2, Ω_6=3.057 × 10^{-20}cm^2 for the BZMD1.0 glass. However, the Ω_2 values are found to be higher than the Ω_4 and Ω_6 intensity parameter values and the trends $\Omega_2>\Omega_4>\Omega_6$ for all the prepared glasses. The JO parameter values are also presented in **TABLE 1.** The spectroscopic quality factor is the significant parameters used to relate the optical quality of the prepared glasses and is calculated from (Ω_4/Ω_6) ratio values. Among the prepared glasses, BZMD1.0 glass (2.107) appears to be a better optical glass. The higher spectroscopic quality factor predicts higher stimulated emission cross-section among the prepared glasses.

Luminescence Studies

The excitation spectrum of BZMD1.0 doped glasses is monitored at 574 nm and is shown in **FIGURE 2.** The excitation spectrum exhibits six bands as $^6P_{3/2}$, $^6P_{7/2}$, $^4P_{3/2}$, $^4F_{7/2}$, $^4G_{11/2}$ and $^4I_{15/2}$. The excitation transitions centered at 384 nm was selected for further characterization of the emission spectra of Dy^{3+} doped fluoroborate glasses. The luminescence spectra of the Dy^{3+} doped fluoroborate glasses are recorded at room temperature in the wavelength range 400–700 nm as shown in **FIGURE 3.** The luminescence spectra exhibit two strong emission band peaks at 476 nm and 571 nm corresponding to $^4F_{9/2}\rightarrow{}^6H_{15/2}$ (blue) magnetic dipole and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ (yellow) electric dipole transitions respectively. In the present work, the existence of asymmetric nature of the host glass network environment around Dy^{3+} ions was confirmed through the observation of higher intensity of $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition than that of $^4F_{9/2}\rightarrow{}^6H_{15/2}$ transitions. The effect of Dy^{3+} ion concentration on the luminescence spectra of all prepared glasses are noticed.

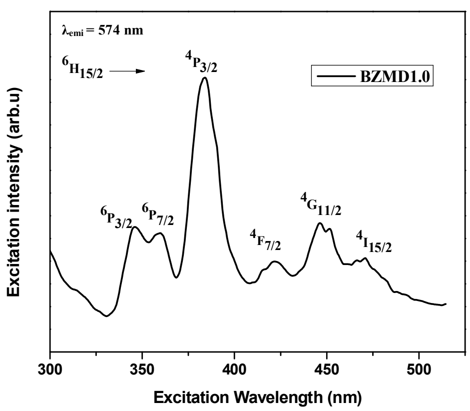

FIGURE 2. Excitation spectrum of the Dy^{3+} BZMD1.0 glass

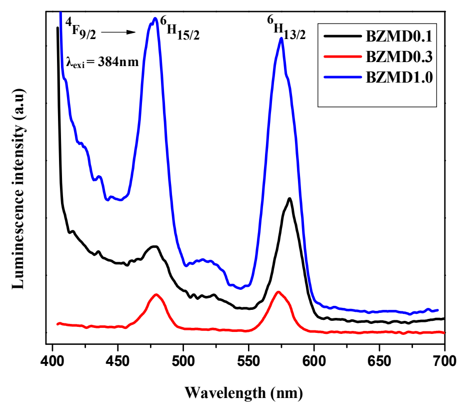

FIGURE 3. Luminescence spectra of the Dy^{3+} doped fluoroborate BZMDx glasses

TABLE 2. The effective bandwidth ($\Delta\lambda_{eff}$ nm), transition probability (A), calculated and experimental branching ratios (β_R) and stimulated emission cross-section ($\sigma_P^E \times 10^{-22}$ cm^2) for the $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transitions of the Dy^{3+}doped fluoroborate glasses

Glass code	$^4F_{9/2}\rightarrow{}^6H_{15/2}$					$^4F_{9/2}\rightarrow{}^6H_{13/2}$				
	$\Delta\lambda_{eff}$	A	β_R(cal)	β_R(exp)	σ_P^E	$\Delta\lambda_{eff}$	A	β_R(cal)	β_R(exp)	σ_P^E
BZMD0.1	13.984	173.47	0.185	0.476	3.457	8.233	551.79	0.590	0.462	40.489
BZMD0.3	7.935	184.25	0.170	0.506	6.474	7.430	667.19	0.617	0.494	51.065
BZMD1.0	14.760	315.88	0.195	0.552	5.800	9.938	975.42	0.602	0.448	55.472

Radiative Properties

The radiative properties such as the transition probability (A), branching ratios (β_R) and stimulated emission cross-section ($\sigma_P^E \times 10^{-22}$ cm^2) for the emission transition $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ of the Dy^{3+} ions have been calculated using the JO intensity parameters. The calculated radiative properties of the prepared glasses are presented in **TABLE 2.** The branching ratios (β_R) and stimulated emission cross-section ($\sigma_P^E \times 10^{-22}$ cm^2) values are important parameters for the potential laser applications [6]. It is observed from the **TABLE 2** that the experimental and calculated (β_R) values are noticed to be higher for the $^4F_{9/2}\rightarrow{}^6H_{13/2}$ (electric dipole) transition and lower for $^4F_{9/2}\rightarrow{}^6H_{15/2}$ (magnetic dipole) transition for all the prepared glasses. The higher magnitude of the stimulated emission cross-section (σ_P^E) is an indication for efficient laser emission. Among the prepared glasses, BZMD1.0 glass posses higher (σ_P^E) value (55.472×10^{-22}cm^2) which correspond to the $^4F_{9/2}\rightarrow{}^6H_{13/2}$ emission transition. It is observed from the tabulated results that, among the prepared glasses, BZMD1.0 glass is found to be more suitable for developing visible lasers applications.

Yellow to Blue (Y/B) Intensity Ratio and Stimulation of White Light

The proper combination of the yellow and blue light can produce white light emission. The Yellow to blue ratio (Y/B) of prepared glasses have been calculated and presented in **TABLE 1**. The Y/B ratio of the BZMD0.1, BZMD0.3 and BZMD1.0 glasses are estimated to be 1.212, 1.194 and 1.201 respectively.

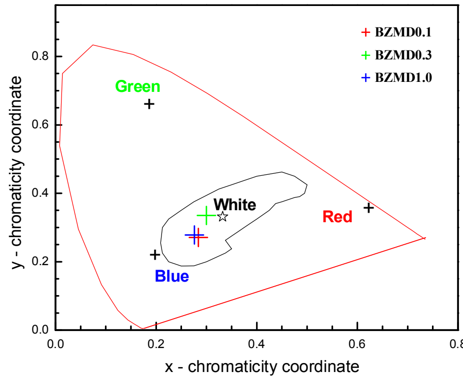

FIGURE 4. CIE diagram of Dy^{3+}doped fluoroborate BZMDx glasses

In order to find out the color coordinates of the prepared glasses, the emission spectra have been analyzed using the frame work of CIE (Commission International deI'Eclairage) 1931 chromaticity diagram [7]. The chromaticity coordinates are found to be (0.284, 0.271), (0.300, 0.335) and (0.276, 0.278) corresponding to the BZMD0.1, BZMD0.3 and BZMD1.0 glasses respectively. It is found from the **FIGURE 4** that the color coordinates of all the prepared glasses lie in the white light region. Hence all of these prepared glasses can be used as white light emitting materials.

CONCLUSION

The Dy^{3+}-doped fluoroborate glasses are prepared by melt quenching technique and investigated through the optical absorption and photoluminescence for White LED's application. The bonding parameters of the prepared glasses have been studied and the negative sign of δ indicates the ionic nature of the Dy^{3+}-O bond in the prepared glasses. The oscillator strengths and the JO intensity parameters Ω_λ (λ=2,4,6) have been calculated for the prepared glasses and it follows the trends as $\Omega_2>\Omega_4>\Omega_6$ uniformly for all the glasses. From the emission spectra the effect of Dy^{3+} ion concentration on the Y/B intensity ratios and the CIE chromaticity coordinates have been calculated for the generation of white light.

REFERENCES

1. S. Arunkumar, G. Venkataiah, K. Marimuthu, Spectrochim. Acta Part A, **136**, 1684–1697 (2015).
2. I. Arul Rayappan, K. Selvaraju, K. Marimuthu, Physica B, **406**, 548–555 (2011).
3. R. Vijayakumar, G. Venkataiah, K. Marimuthu, J. Alloys Compd. **652**, 234–243 (2015).
4. B.R. Judd, Phys. Rev. **127**, 750–761 (1962).
5. G.S. Ofelt, J. Chem. Phys. **37**, 511–520 (1962).
6. P. Babu, C.K. Jayasankar, Opt. Mater. **15**, 65–79 (2000).
7. G. Venkataiah, C.K. Jayasankar, J. Mol. Struct. **1084**, 182–189 (2015).