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Synthesis Structural and Optical Studies on Composition Dependent Dy^{3+} doped Fluoroborate Glasses

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Abstract

The Dy^{3+} ions doped fluoroborate glasses with composition $39B_2O_3$ + 20ZnO + 20NaF + $20XCO_3$ + $1Dy_2O_3$ in mol% (where X = Li_2, Mg) have been prepared by melt quenching technique and characterized through XRD, FTIR, absorption and luminescence spectral analysis. The XRD measurement was made to examine the amorphous nature of the prepared glasses. The stretching and bending vibrations of various functional groups have been investigated through FTIR spectra. The bonding parameters (β and δ) were calculated from the absorption spectra to understand the nature of bonding of chemical environment in the prepared glasses. The Judd-Oflet (JO) intensity parameters (Ω_λ (λ=2,4,6)) were determined from the measured oscillator strength of various absorption bands in order to study the symmetry around the RE ion site and used to compute the radiative properties such as emission band position(λ_P) effective bandwidth ($\Delta\lambda_{eff}$), transition probability (A), stimulated emission cross-section ($\sigma^E{}_P$) and branching ratios (β_R). The emission spectra exhibit two emission bands $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^6H_{13/2}$ corresponding to nblue and yellow emission under 374 nm excitation. The emission intensities were calculated and compared with the reported literature.

Keywords: Bonding parameters, Ligand field effect, Judd-Oflet parameter, Emission, Radiative properties.

1. Introduction

The development of the new luminescent materials with appropriate composition doped with RE^{3+} ions is of interest for understanding the electronic excitation and relaxation phenomena RE ions in the chosen glass matrices [1-5]. The choice of choosing host matrix is an important key to improve the spectroscopic behavior of RE ions for various applications such as optical storage solid state lighting, updown conversion display devices etc., [6-8]. Among various glass host matrices borate based glasses are widely preferred due to its high transparency, low melting point, high rare earth ion solubility and good infrared transmission [9,10]. Fluroborate glasses are highly preferred because of its high ionic conductivity, short-range order around network forming boron, high chemical durability and lower phonon energy (≤600cm^{-1}) which reduces the non-radiative rates thus increasing the luminescence quantum efficiency [11]. Moreover these fluroborate glasses are favorable hosts to energy transfer and excited state absorption processes, which give rise to frequency up/down conversion mechanisms [12-15]. Among the RE ions, Dy^{3+} ion plays a major role in the production of white light emitting luminescent materials because it can be easily excited by the commercially available UV or blue LEDs due to its several excitation bands in the

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range 320–480 nm [5]. Arul Rayappan et al [6] studied Dy^{3+} concentration effect on structural, thermal and optical behavior of B_2O_3–PbO–PbF_2 glasses and reported the occurrence of luminescence quenching caused by the energy transfer among the Dy^{3+} ions through various cross-relaxation channels. The present work reports the structural and optical behavior of Dy^{3+}doped fluroborate glasses for photonic applications and compared with reported Dy^{3+} doped glasses.

2. Experimental procedure

Dy^{3+} doped BZXD glasses were prepared by conventional melt quenching technique by [5,6]. H_3BO_3, ZnO, NaF, Li_2CO_3, $MgCO_3$, Dy_2O_3 were taken as precursors. About 8g batch of relevant compositions were mixed and grinded in an agate mortar then it's heated up to 950 °C for 45mins with periodic stirring. The melt was allowed to sudden quenching onto a preheated brass plate and then annealed at 350° C for 7 hrs to remove the thermal strains. X-Ray Diffraction pattern was recorded using JEOL 8030 X-ray diffractometer. FTIR spectra have been recorded using Perkin –Elmer paragon 500 FTIR spectrometer. The absorption spectra were recorded using CARY 500 spectrophotometer. Luminescence spectra of the prepared glass samples were measured using LS45 Spectrophotometer. The other physical properties of the Dy^{3+}: BZXD glasses were calculated using the expression given in the literature and are given in table 1.

Table 1. Physical properties of Dy^{3+}:BZLD glasses

Physical Properties	BZLD	BZMD
Density ρ (g/cm^3)	3.3246	3.6076
Refractive index n_d (nm)	1.589	1.602
REconcentration N (10^{20} ions/cm^3)	5.9501	6.2620
Polaron radius r_p(A˚)	479.05	4.7096
Inter ionic distance r_i(A˚)	118.89	11.688
Field strength F (10^{14} cm^{-2})	2.1222	2.1958
Polarizability (α_e)10^{-22} cm^3	1.3528	1.3084
Molar refractivity R_m (cm^3)	8.1853	7.9166
Dielectric constant (ε)	2.5249	2.5664
Reflection losses R (%)	5.1756	5.3527

3. Result and discussion

3.1. XRD and FTIR spectra

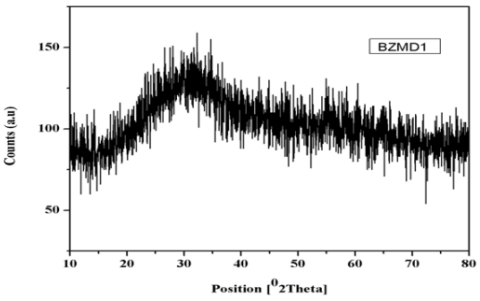

Figure 1. XRD pattern of Dy^{3+}:BZMD glass

Fig. 1 shows the x-Ray diffraction pattern of BZMD glass and it exhibit a broad diffuse scattering at lower angles, suggesting structural disorder which confirms the amorphous nature of the prepared glass. Fig. 2 shows the FTIR spectra of the glasses and their corresponding band position along with the assignment are presented in table 2. The peaks observed around 2800 and 2900 cm^{-1} are characteristic of hydrogen bonds in the glass systems. The peaks around 1409cm^{-1} are assigned to

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B-O vibrations and the bands around this value for the different glass systems are found to be broader [7]. The broad peak around 1023 cm^{-1} is due to B-O vibrations associated with BO_4 units and B-O-B linkages exhibit a band around 721 cm^{-1} [8].

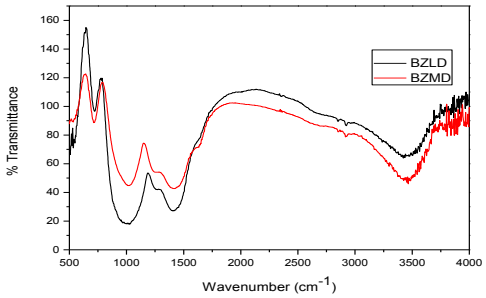

Figure 2. FTIR spectra of Dy^3:BZxD glasses

Table 2: Band assignments (cm^{-1}) of Dy3:BZxD glasses

BZLD	BZMD	[7]	[8]	Assignments
3445	3447	3430	3449	O-H stretching
2920	2907	2924	2922	Hydrogen bonding
2848	2353	1630	2845	Hydrogen bonding
1409	1414	1421	1348	B-O⁻ vibrations
1023	1022	1084	1011	B-O vibrations
721	790	710	695	Pyroborate Group

3.2. Absorption spectra

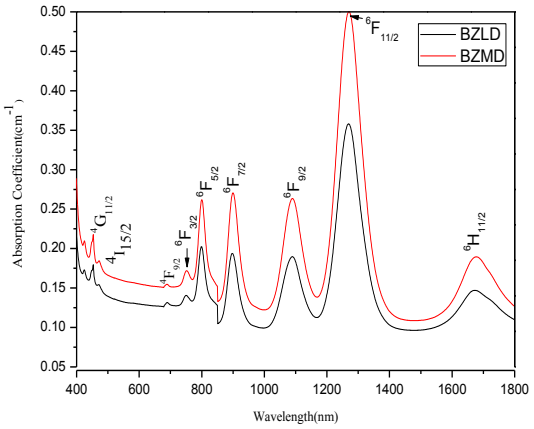

Figure 3. Absorption spectra of Dy^{3+}: BZXD glasses

Figure 3 shows the UV-Vis-NIR absorption spectra of Dy^{3+} doped BZXD glasses and the observed band positions are presented in Table 3. The absorption spectra exhibit 9 absorption bands which originates from $^6H_{15/2}$ ground state to various excited $^6H_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$, $^4F_{9/2}$, $^4I_{15/2}$, $^4G_{11/2}$, $^6P_{5/2}$ states of the Dy^{3+} ions. The intensity of the $^6H_{11/2}$ absorption transitions is higher than other transition due to its hypersensitive nature. It is observed from the figure 3 that, the band position and intensities of the absorption transitions undergoes small variation due to the Nephlauxetic effect. Thus influence of ligand environment on the RE energy levels can be measured by Nephelauxetic intensity ratio and bonding parameter of the prepared samples using the expression given on the literature [5,7,8] The bonding will be covalent or ionic depending upon the positive and negative sign of δ and the measured β and δ values are presented in table 3. The negative values of δ values indicates the ionic nature of the prepared glasses.

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Table 3. Observed band positions (cm^{-1}), β and δ of Dy^{3+} doped fluoroborate glasses

Transition $^6H_{15/2}\rightarrow$	Energy		Reported values [7,9]		Aqua [8]
	BZLD	BZMD			
$^6H_{11/2}$	5977	5949	5968	5974	5850
$^6F_{11/2}$	7874	7874	7867	7794	7700
$^6F_{9/2}$	9174	9158	9187	9166	9100
$^6F_{7/2}$	11148	11099	11102	11161	11000
$^6F_{5/2}$	12516	12484	12498	12531	12400
$^6F_{3/2}$	14440	13333	13337	13332	13250
$^4F_{9/2}$	21231	21231	21070	21132	21100
$^4I_{15/2}$	22075	22075	22051	22075	22100
$^4G_{11/2}$	23585	23529	------	23830	23400
β	1.010	1.007	-	-	-
δ	-1.040	-0.793	-	-	-

3.3. Oscillator strength and Judd-Oflet analysis

The spectral intensity of the absorption bands of RE ions are analysed based on the calculated and experimental oscillator strength (f_{exp}) values and are measured using the expressions reported in literature [13] and are presented in table 4. The observed experimental oscillator strength are found to be similar with the f_{exp} of other reported papers [10], [7] and [8]. Generally, JO parameters provide information about the nature of the bond between RE ions and surrounding ligand as well as the symmetry of the environment around the RE ions. The spectral intensity of $^6F_{11/2}$ hypersensitive transition is found to be more than other transitions.

Table 4. Experimental and calculated oscillator strength ($\times 10^{-6}$) of Dy^{3+} doped BZLD and BZMD glass

$^6H_{15/2}\rightarrow$	BZLD		BZMD		1.0LBTPD [7]		Dy:LiLTB [11]	
	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}
$^6H_{11/2}$	0.95	0.79	1.52	1.58	1.64	1.93	0.90	1.26
$^6F_{11/2}$	5.11	5.13	6.86	6.85	11.7	11.6	7.93	7.88
$^6F_{9/2}$	1.89	1.83	2.61	2.61	4.05	4.19	2.43	2.55
$^6F_{7/2}$	1.80	1.27	2.50	2.56	3.64	3.11	2.26	1.90
$^6F_{5/2}$	1.07	0.53	1.67	1.29	1.56	1.36	1.67	0.83
$^6F_{3/2}$	0.20	0.10	0.21	0.24	0.35	0.25	0.23	0.16
$^4F_{9/2}$	0.25	0.10	0.30	0.20	0.25	0.23	-	-
$^4I_{15/2}$	0.15	0.27	0.63	0.55	0.78	0.64	-	-
$^4G_{11/2}$	0.23	0.07	0.27	0.04	-	-	-	-
N	9		9		8		6	
σ_{rms}	±0.21		±0.15		±0.24		±0.41	

The JO intensity parameters of the present Dy^{3+} doped glasses were calculated using leat square fitting method followed by the literature [12,15] and are presented in table 5 along with the reported Dy^{3+} doped glasses. The values of Ω_2 is very sensitive to the local environment of the RE ions and often gives information about the symmetry of the coordination structure, polarizability of ligands and the nature of the RE–O bonding in the ligand field [31]. The Ω_4 parameters is related to the bulk properties and Ω_6 is inversely related to the rigidity of the medium and also affected by the vibronic transitions of the RE ions. It is observed from table 5 that, the JO parameters follow the trend as $\Omega_2>\Omega_4>\Omega_6$ for BZLD and $\Omega_2>\Omega_6>\Omega_4$ for BZMD glasses. The JO intensity parameters of the title glasses are found to be similar and comparable to the reported literature [6,8,11,14].

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Table 5. JO intensity parameters of Dy^{3+}:BZXD glasses

Glass code	JO Parameters Ω_λ ($\times10^{-20}cm^2$)				Ref
	Ω_2	Ω_4	Ω_6	Trends	
BZLD	5.12	1.98	1.27	$\Omega_2>\Omega_4>\Omega_6$	Present
BZMD	7.71	1.21	3.06	$\Omega_2>\Omega_6>\Omega_4$	Present
L6BD	12.8	3.47	3.43	$\Omega_2>\Omega_4>\Omega_6$	[8]
1DPTFB	7.38	1.65	2.30	$\Omega_2>\Omega_6>\Omega_4$	[11]
LBZLB	14.4	5.23	5.71	$\Omega_2>\Omega_6>\Omega_4$	[14]

3.4. Luminescence Spectra: Radiative properties

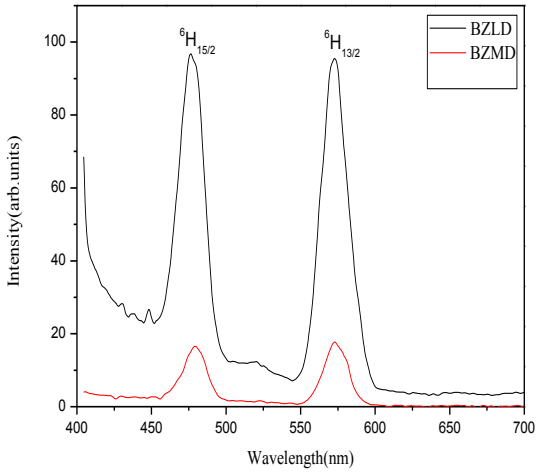

Figure 4. Emission spectra of Dy^{3+}:BZLD &BZMD glasses

The luminescence spectra of the Dy^{3+}: BZXD glasses were recorded at 374 nm excitation and the same is presented in Fig. 4. The luminescence spectra exhibit two emission peaks at 474 and 575nm corresponding to $^4F_{9/2}\rightarrow{}^6H_{15/2}$ (blue) and $^6H_{13/2}$ (yellow), transitions respectively. The $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition is hypersensitive electric dipole transition ($\Delta J=\pm2$) which has been strongly influenced by the coordination environment. The $^4F_{9/2}\rightarrow{}^6H_{15/2}$ transition is a magnetic dipole transition ($\Delta J=0, \pm1$ but $0\leftrightarrow0$ forbidden) and less sensitive to the coordination environment. In Appropriate combination of the dominant emission transitions corresponding to the blue ($^4F_{9/2}\rightarrow{}^6H_{15/2}$) and yellow ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) bands exhibit white light emission [36]. The $^4F_{9/2}\rightarrow{}^6H_{13/2}$ emission transition possess higher intensity compared to the other transitions thus indicates the higher asymmetry possessed by the Dy^{3+} ions with its surrounding ligands.

The JO intensity parameters (Ω_2 ,Ω_4 ,Ω_6) and refractive index were used to obtain the radiative parameters like effective bandwidth ($\Delta\lambda_{eff}$, nm), transition probability (A s^{-1}), calculated and experimental branching ratios (β_R) and stimulated emission cross-section ($\sigma_p\times10^{-22}$ cm^2) for the emission transitions $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ of Dy^{3+}doped fluoroborate glasses. The radiative properties of Dy^{3+}:BZXD glasses along with the reported literatures are presented in table 6. The branching ratio (β_R) is a significant parameter for the fabrication of laser devices, because it characterizes the possibility of attaining stimulated emission from any particular transition of the studied glasses. The experimental branching ratio values (β_{exp}) are calculated using the relative intensities of the individual peaks to that of the total intensity of the emission peaks and are found to be comparable to the calculated (β_{cal}) values obtained within the frame work of JO theory. It is observed from table 6 that, the branching ratio of the $^4F_{9/2}\rightarrow{}^6H_{13/2}$ emission transition is found to be higher than the other emission transitions. The stimulated emission cross-section is an important parameter for the design of low threshold and high gain lasers. The effective line width ($\Delta\lambda_{eff}$) of the $^4F_{9/2}\rightarrow{}^6H_{13/2}$ emission transition indicates the sharpness of the transition compared to other transitions and is found to be very low compared to the reported Dy^{3+} doped glasses [16]. Thus the higher σ_p and small $\Delta\lambda_{eff}$ values suggest that the $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition is most potential for laser

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action. Among the observed transitions, the σ_p^E value is found to be higher for the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition. The higher σ_p^E cross-section of BZMD glass is suggested for low-threshold, high gain applications and are utilized to obtain continuous wave laser action [17].

Table 6. The values of λ_P(nm), $\Delta\lambda_{eff}$ (nm), A (s^{-1}), β_R and σ_p^E($\times 10^{-22}$ cm^2) of Dy^{3+}doped BZXD glasses

Parameters		BZLD	BZMD	[8]	[13]
$^4F_{9/2} \rightarrow {}^6H_{15/2}$	λ_P	474	478.5	479	472
	$\Delta\lambda_{eff}$	8.7473	0.5618	7	9.7506
	A	119.83	250.97	267.47	75.11
	β_R(cal)	0.1436	0.1857	0.201	0.0911
	β_R(exp)	0.3916	0.5618	0.306	0.2805
	σ_p^E	3.6340	6.5930	13.107	2.44
$^4F_{9/2} \rightarrow {}^6H_{13/2}$	λ_P	575	572.5	574	571
	$\Delta\lambda_{eff}$	6.2598	0.4382	15	6.65
	A	516.20	848.03	917.29	726.19
	β_R(cal)	0.6184	0.6275	0.688	0.6685
	β_R(exp)	0.6083	0.4381	0.656	0.6616
	σ_p^E	47.373	81.786	37.076	69.5

4. Conclusion

The Dy^{3+}: BZXD(X= Li_2, Mg) fluroborate glasses have been synthesized and their structural and optical behavior were studied. The amorphous nature of glasses were confirmed through XRD. The FTIR spectra of both BZLD and BZMD reveal the presence of various stretching units of borate networks along with the O-H stretching and bending vibrations. From the optical absorption spectra it is clear that Dy^{3+}ions exhibit a strong ionic nature. The oscillator strength and JO intensity parameters (Ω_λ, λ=2, 4,6) have been calculated and it follows the trend $\Omega_2 > \Omega_4 > \Omega_6$ for BZLD and $\Omega_2 > \Omega_6 > \Omega_4$ for BZMD glasses. The radiative properties such as effective bandwidth, transition probability, calculated and experimental branching ratios and stimulated emission cross-Section for various transitions of Dy^{3+} ions were calculated and compared with the literatures. The higher values of σ_p^E and β_R of the BZMD glass implies its suitability for the fabrication of highly monochromatic yellow laser applications [36].

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