Synthesis and Optical Studies on Concentration Dependent Dy^{3+} Doped Sodium-borophosphate Glasses

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Abstract. The Dy^{3+} doped sodium borophosphate glasses with the chemical compositions of(50-x) H_3BO_3+10P_2O_5+10ZnO+15Na_2CO_3+15NaF+xDy_2O_3 in wt% (where X= 0.1 and 1.0) have been prepared by conventional melt quenching technique. The structural properties of the prepared glasses were studied through XRD and the spectroscopic behaviors characterized through absorption and emission spectra. XRD spectral analysis conform the amorphous nature of the prepared glasses. The ionic natures of the metal-ligand bond in the prepared glasses were evaluated by the bonding parameters (β and δ) from absorption spectra. The J-O parameter (Ω_2, Ω_4 and Ω_6), the theoretical and experimental oscillator strength were determined and reported. The CIE (1931) chromaticity diagram for various pumping wavelengths of emission spectra has been plotted and found that the prepared glasses suitable for WLED applications.

INTRODUCTION

Modern technology in the materials science are focused their attention on lasing device fabrication, color display devices and photonics applications. Now a days there has been a prime importance in the fabrication of RE doped glasses and serves the excellent activator due to their characteristics 4f - 4f or 5f – 4f emission transition[1]. Among the different RE ions,Dy^{3+} ion is the best suited RE for understanding the luminescent properties as a function of concentration of RE and composition of the glass matrix, due to the optical transition consisting of blue $^4F_{9/2}\rightarrow{}^6H_{15/2}$~ 484 nm, yellow $^4F_{9/2}\rightarrow{}^6H_{13/2}$~ 574 and red $^4F_{9/2}\rightarrow{}^6H_{11/2}$~ 682 nm emission in the visible and NIR region. The great amount of investigation has been carried out and studied through absorption and luminescence properties which strongly depends the glass composition. The glass composition decided the quality of the RE doped glasses which are influenced by the ligand field of the surrounding RE ions. From the different glass hosts including phosphate, borate, silicate and fluoride has been termed as the matrix materials along with the RE for the improving the glasses in various application. Borate and phosphate having their unique properties. But, in order to avail the both advantages of borate and phosphate combined together and formed the borophosphate glasses that possess the good optical quality, good thermal and mechanical stability, good rare earth ion solubility, large emission cross-section and narrow emission bandwidth [2]. The higher phonon energy of the borophosphate glasses lead to have non radiative emission by the multiphonon relaxation. In order to overcome from this difficulties the fluride is added to this network to reduce the phonon energy. To avoid the hydroscopic nature ZnO added in the network and also increasing glass forming tendency.From these idea the aim of the present paper is to (i) examine the structure of the prepared glass through XRD; (ii) calculate the bonding parameter; (iii) find the oscillator strength (iv) evaluate the JO parameters and to compare the trends of JO parameters with respect to other Dy^{3+} doped glasses (v) draw the CIE chromaticity diagram from the emission spectra.

EXPERIMENTAL

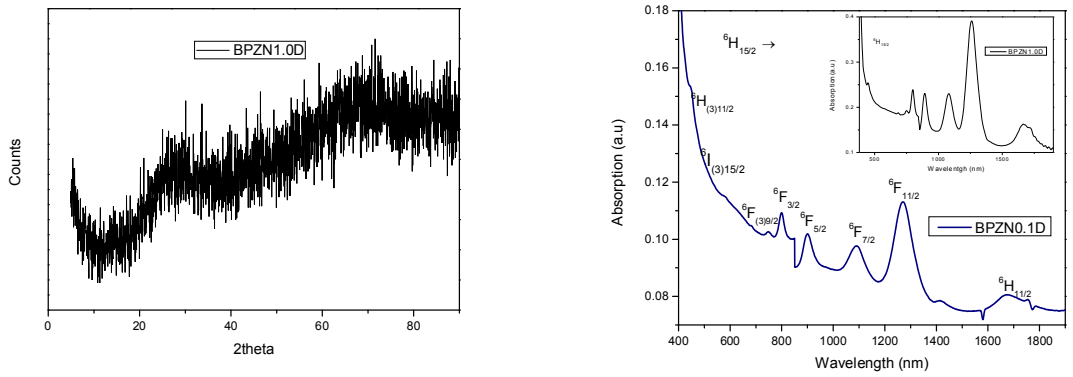
The Dy^{3+} doped Sodium-borophosphate Glasses were preparedusing conventional melt quenching technique following the procedure reported in literature [3] and the prepared glass samples were labeled as BPZN0.1D and

BPZN1.0D respectively. The XRD of prepared glasses were recorded using XPERT-PRO X-ray diffractometer with CuKα radiation. Absorption spectra were recorded using Perkin Elmer Lambda 35 UV–VIS-NIR spectrometer in the wavelength range 300–2000 nm with a spectral resolution of 0.1 nm. The luminescence spectra were carried out using Perkin Elmer LS55 spectrometer in the wavelength range 375–700 nm with a resolution of 0.1 nm.

RESULTS AND DISCUSSION

XRD Spectra

The X-ray diffraction (XRD) pattern has been recorded in the range $10^0 \leq \theta \leq 80^0$. The XRD pattern confirms the amorphous nature of the prepared glasses. Because it exhibits broad defused scattering at lower angles, suggesting the long range structural disorder are noted from the **FIGURE 1.** (a).



(a) **(b)**

FIGURE 1. (a) XRD pattern of the Dy^{3+} doped Sodium-borophosphate glasses, (b) UV-Vis-NIR absorption spectra of Dy^{3+} doped Sodium-borophosphate glasses

Absorption Spectra

FIGURE 1. (b) the UV-Vis-NIR absorption spectra of the Dy^{3+} doped Sodium-borophosphate Glasses are recorded at room temperature in the wavelength region between 300 nm and 2000 nm and it exhibits 9 absorption transition of Dy^{3+} ions from the ground state $^6H_{15/2}$ to various excited energy levels such as $^6H_{11/2}$, $^6F_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$, $^4F_{(3)9/2}$, $^4I_{(3)15/2}$, and $^4H_{(4)11/2}$ with a slight different in their intensity. The absorption band at around 1270 nm corresponds to the hypersensitive transitions $^6H_{15/2} \rightarrow {}^6F_{11/2}$ possess higher absorption intensity than the other transitions and obey the selection rules ($\Delta S = 0$) [4]. The positive or negative sign of the δ value is used to identify the nature weather it is covalent or ionic nature. The δ values are found to be-1.2075and-1.4886corresponding to BPZN0.1D and BPZN1.0D respectively and are presented in **TABLE 1.** The negative δ values indicate the ionic nature of the Dy^{3+} metal-ligand bond.

TABLE 1. Bonding parameters (β and δ), Judd-Ofelt intensity parameters (Ω_λ, 10^{-20} cm^2) for the Dy^{3+} doped Sodium-borophosphate glasses.

Parameters	BPZN0.1D	BPZN1.0D
B	1.0122	1.0151
Δ	-1.2075	-1.4886
Ω_2	0.0626	0.7642
Ω_4	0.0187	0.1061
Ω_6	0.0254	0.2329
Ω_4 / Ω_6	0.7359	0.4556

Oscillator strengths and Judd-Ofelt parameters

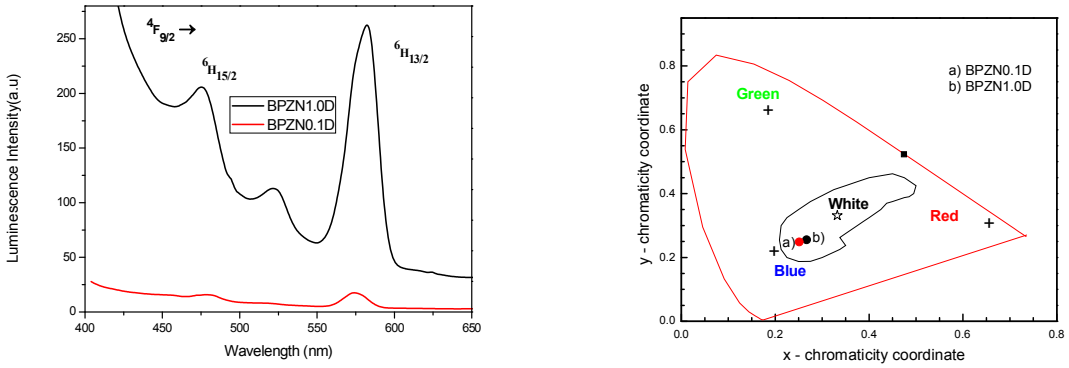
The experimental and calculated oscillator strengths of the f-f induced electric dipole transition of each band of the observed transitions were determined by the least square fitting procedure [3] from the absorption energy levels and refractive index. The root mean square deviation δ_{rms} values were also calculated to determine the quality of the fit between f_{exp} and f_{cal} values of the absorption transition are presented in **TABLE 2**. The small rms deviations δ_{rms} indicates a good fit between experimental and calculated values. The JO parameters [5,6] follows the trend as $\Omega_2>\Omega_6>\Omega_4$for all the prepared glasses and the spectroscopic quality factor ($\Omega_4/\ \Omega_6$) is a measure of the optical quality. The higher $\Omega_4/\ \Omega_6$ value implies the feasibility of the prepared glasses for the potential Laser applications. It is observed from these results that among the prepared glasses, BPZN0.1D glass and (0.7359)appears to be a better optical glasses. The larger spectroscopic quality factor predicts higher stimulated emission cross section among the prepared glasses.

TABLE 2. The experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths (10^{-6}), number of transitions (N) and rms deviation(σ) of the Dy^{3+} doped sodium-borophosphate glasses

Transition from $^6H_{15/2}\rightarrow$	BPZN0.1D		BPZN1.0D	
	f_{exp}	f_{cal}	f_{exp}	f_{cal}
$^6H_{11/2}$	0.0100	0.0109	0.1210	0.1226
$^6F_{11/2}$	0.0660	0.0659	0.6210	0.6207
$^6F_{9/2}$	0.0250	0.0253	0.1980	0.1936
$^6F_{7/2}$	0.0190	0.0181	0.1620	0.1861
$^6F_{5/2}$	0.0060	0.0077	0.1460	0.0922
$^6F_{3/2}$	0.0190	0.0150	0.0110	0.0173
$^6F(3)_{9/2}$	0.0080	0.0140	0.0060	0.0144
$^4I(3)_{15/2}$	0.0080	0.0360	0.0150	0.0418
$^4H(4)_{11/2}$	0.0040	0.0010	0.0080	0.0041
N		9		9
σ		±0.007		±0.022

Luminescence Spectra and CIE Chromaticity Diagram

FIGURE 2a shows the photoluminescence spectra for the different concentration of Dy^{3+} doped Sodium-borophosphate glasses were recorded in the region 400–700 nm with an excitation at 384 nm. Two luminescence bands are observed which is corresponding to the magnetic dipole ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) and electric dipole ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) transitionsof Dy^{3+} doped sodium-borophosphate glasses. The main band is located at the blue band at ~ 479 nmand yellow band at ~ 574 nm are the predominant transitions [7]. $^4F_{9/2} \rightarrow {}^6H_{13/2}$transition is the hyper sensitive transition and it intensitystrongly depends on the host whereas intensity of the $^4F_{9/2} \rightarrow {}^6H_{15/2}$transition is sensitive to the host. No change in the shape or the peak position of the broad emission are observed.The **FIRURE 2b** shows the CIE 1931 chromaticity diagram of the prepared glasses. The obtained x, y coordinates are found to be (0.25, 0.24), and (0.26, 0.25) correspond to the BPZN0.1D and BPZN1.0D glasses respectively. It is observed from the CIE diagram that x, y coordinates of all the prepared glasses are found to lie in the white light region of the CIE diagram and thus reveal its suitability for white light applications.



(a) (b)

FIGURE 2.a)Emission spectra of Dy^{3+} doped sodium-borophosphate glasses,b) CIE Color Chromaticity diagram of the Dy^{3+} doped sodium-borophosphate glasses

CONCLUSION

The Dy^{3+} doped sodium-borophosphate glasses were prepared and their structural and optical properties were studied through XRD, absorption and luminescence spectral measurements. The XRD pattern confirms the amorphous nature of the prepared glasses. Negative δ values indicate the ionic nature of the Dy^{3+}– O bond in the prepared glasses.The JO parameters follows the trend as $\Omega_2>\Omega_6>\Omega_4$for all the prepared glasses. The x, y coordinates of the prepared glasses are located in the white light region of the CIE diagram and thus suggests their suitability for white LED's applications.

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