Physica B 457 (2015) 287–295

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

White light simulation and luminescence studies on Dy^{3+} doped Zinc borophosphate glasses

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ARTICLE INFO

Article history:
Received 11 August 2014
Received in revised form
30 September 2014
Accepted 3 October 2014
Available online 13 October 2014

Keywords:
Judd–Ofelt parameters
Optical bandgap
Luminescence
Radiative properties
Cross-relaxation

ABSTRACT

The Dy^{3+} doped Zinc borophosphate glasses with the chemical composition $(79\text{-}x)B_2O_3 + xP_2O_5 + 10Li_2O + 10ZnO + 1Dy_2O_3$ (where $x=0$, 10, 20, 30 and 50 in wt%) have been prepared by melt quenching technique. The prepared glass samples were characterized through optical absorption, emission and decay measurements. The bonding parameters, optical band gap and Urbach's energy values were calculated from the optical absorption spectra to explore the bonding nature of the Dy–O metal ligand and electronic band structure of the studied glasses. Judd–Ofelt (*JO*) intensity parameters were calculated from the absorption spectra by using the JO theory and it gives information about symmetry of the ligand environment around the Dy^{3+} ion site. The *Y*/*B* intensity ratio and radiative properties were obtained from the emission spectra and the results were compared with the reported literature. The *x*, *y* chromaticity color coordinates of the studied glasses were analyzed using a CIE 1931 color chromaticity diagram and found that the *x*, *y* coordinates lie in the white light region. The decay curve measurements of the prepared glasses exhibit non-exponential behavior and are well fitted to Inokuti–Hirayama (IH) model to understand the energy transfer mechanism between Dy^{3+} ions. The *Q*, R_0 and C_{DA} values of the prepared Dy^{3+} doped glasses were obtained from the IH model and the results were discussed and compared with the reported literature.

1. Introduction

Recently, many researchers focus on mercury free fluorescent lamps for general lighting purpose to reduce the usage of environmentally insecure materials and the hazardous ingredients. The light emitting diodes (LEDs) are found to be better alternative to the argon mercury discharge fluorescent lamps for general lighting purpose [1]. Especially, White-Light Emitting Diodes (W-LEDs) made remarkable breakthrough in the field of solid state lighting technology due to their potential applications in solid state lasers, domestic lamps, automobile headlights, full-color displays, enhanced solar cells and cellular phone illuminations etc. [2–4], and play an important role in sinking of global electricity conception. Normally, the commercial W-LEDs were obtained by coating the yellow phosphors on the surface of blue LED chip which could cause poor white light emission, short lifetime and show deviations in emission wavelength due to inhomogeneous phosphor coating. Also, it exhibit contrast in Yellow to Blue (*Y*/*B*) intensity ratio which in turn leads to have unwanted yellowish blue or bluish yellow emission. In order to overcome these difficulties and to get bright white light emission, many researchers give much attention to trivalent Rare Earth (RE^{3+}) ions doped glass materials as well as crystals. RE ion doped glasses exhibit homogeneous luminescence, high thermal and mechanical stabilities and can be produced in low cost when compared with phosphor coated blue LEDs.

Among the several RE ions, the Dy^{3+} ion is prominent for W-LED applications due to its two intense emission bands, one in yellow (~574 nm) region corresponds to the electric dipole transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$ which is hypersensitive in nature and another one in the blue (~481 nm) region corresponds to the magnetic dipole transition $^4F_{9/2} \rightarrow {}^6H_{15/2}$. Also, it exhibits feeble red emission around 662 nm corresponding to the $^4F_{9/2} \rightarrow {}^6H_{11/2}$ transition [5]. The generation of white light from the Dy^{3+} doped glass materials can be achieved by adjusting these yellow to blue integral intensity ratios because the line joining blue and yellow wavelength is usually passes through the white light region in the CIE 1931 (Commission International de l'Eclairage) color chromaticity diagram. Furthermore, the *Y*/*B* ratio can be optimized by choosing appropriate RE ion concentration, glass composition and the excitation wavelength.

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http://dx.doi.org/10.1016/j.physb.2014.10.003
0921-4526/

The selection of suitable glass host for the doping of RE ions is essential to ensure its applicability in photonic applications. The addition of borate (B_2O_3) content into the phosphate glass enhances the chemical durability, thermal and mechanical stabilities and modify the glass structure through cross linked new P–O–B bonds [5,6]. Addition of ZnO into the borophosphate network lead to have unique properties like non-hygroscopic nature, intrinsic emitting properties, large exciton binding energy, non-toxicity and direct wide band gap which make them suitable candidates for non-linear and optoelectronic applications [7]. Therefore, Dy^{3+} doped Zinc borophosphate glass is an interesting subject of glass science. However, few works have been reported on Dy^{3+} doped borophosphate/fluoroborate glasses for white LED applications. Kiran and Suresh Kumar [5] reported the possibility of getting White light emission from Dy^{3+} doped sodium-lead borophosphate glasses under UV light excitation. Luminescence properties of Dy^{3+} doped titanium phosphate glasses were studied and reported by Murthy et al. [8]. Photoluminescence properties of Dy^{3+} ions in fluorophosphate glasses have been studied and reported by Praveena et al. [9]. The spectroscopic behavior of Dy^{3+} ions in fluoroborate glasses were studied by Azeem et al. [10] and reported that the addition of NaF into the borate content enhance the luminescence intensities of Dy^{3+} ions. By considering the practical importance of Dy^{3+} ions doped glasses, it is proposed to explore the optical properties of Dy^{3+} doped Zinc borophosphate glasses in the present work.

2. Experimental

The Dy^{3+} doped Zinc borophosphate glasses were prepared by following the conventional melt quenching technique with the chemical composition $(79-x)B_2O_3+xP_2O_5+10Li_2O+10ZnO+1Dy_2O_3$ (where $x=0$, 10, 20, 30 and 50 in wt%) following the procedure reported in literature [11] and the prepared glass samples were labeled as DyZB0P, DyZB10P, DyZB20P, DyZB30P and DyZB50P respectively. The high purity analytical grade chemicals such as H_3BO_3, $(NH_4)H_2PO_4$, $LiCO_3$, ZnO and Dy_2O_3 obtained from Sigma-Aldrich were used as raw materials to prepare the present glasses.

The refractive index measurements were made employing Abbe refractometer at sodium wavelength (5893 Å) using 1-bromonapthaline as a contact liquid. Based on the Archimedes principle, densities of the title glasses were determined using xylene as an immersion liquid. The physical properties of the present glasses have been calculated and presented in Table 1. The absorption spectral measurements were made with a CARY 500 UV–vis–NIR spectrometer in the wavelength region 375–2500 nm with a spectral resolution of ± 0.1 nm. A Perkin-Elmer LS55 spectrophotometer was used to record the luminescence spectra of the prepared glasses with a spectral resolution of ± 0.1 nm. The decay measurements were made employing the Sciencetech modular spectrometer using a xenon flash lamp as an excitation source. All these measurements were carried out at room temperature (RT) only.

3. Results and discussion

3.1. Absorption spectra and bonding parameters

The optical absorption spectrum of the Dy^{3+} doped Zinc borophosphate glass (DyZB30P) is shown in Fig. 1. The spectrum exhibits 10 absorption bands in the UV–vis–NIR region located at 385, 425, 453, 472, 750, 801, 900, 1091, 1267 and 1677 nm originates due to the electric dipole (ED) transition from the $^6H_{15/2}$ ground state to the various excited states such as $^4I_{13/2}$, $^4G_{11/2}$, $^4I_{15/2}$, $^4F_{9/2}$, $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}$, $^6F_{11/2}$ and $^6H_{11/2}$ respectively. The observed band positions are found to be same irrespective of the change in glass composition and the band assignments were made based on the reported literature [12]. Among all the transitions, $^6H_{15/2}\rightarrow{}^6F_{11/2}$ possess higher intensity and denoted as hypersensitive transition which is sensitive to the host environment and obeys the selection rules $|\Delta S|=0$, $|\Delta L|\leq 2$ and $|\Delta J|\leq 2$. The energy level positions of the Dy^{3+} ions exhibit slight deviation when doped in to the glass materials due to the Nephelauxetic effect. This difference in energy level position gives information about the Dy–O bonding properties and it can be obtained by calculating the bonding parameters ($\bar{\beta}$, δ). The bonding parameter

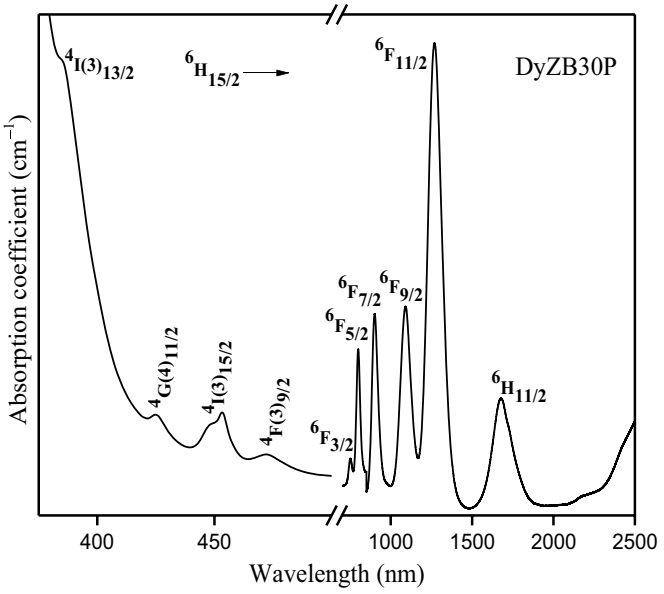

Fig. 1. Absorption spectrum of the Dy^{3+} doped Zinc borophosphate glass.

Table 1
Physical properties of the Dy^{3+} doped Zinc borophosphate glasses.

Physical properties	DyZB0P	DyZB10P	DyZB20P	DyZB30P	DyZB50P
Density, ρ (g/cm^3)	5.455	2.878	3.821	3.572	3.938
Refractive index, n_d (589.3 nm)	1.597	1.589	1.634	1.625	1.594
RE ion concentration, N(10^{20} ions cm^3)	9.679	4.737	5.865	5.135	5.020
Polaron radius, r_p (Å)	8.146	10.338	9.627	10.063	10.139
Inter ionic distance, r_i (Å)	10.109	12.828	11.946	12.487	12.582
Field strength, F (10^{14} cm^{-2})	2.935	1.823	2.102	1.923	1.895
Electronic polarizability, α_e (10^{-22} cm^3)	0.841	1.699	1.456	1.644	1.614
Molar refractivity, R_m (cm^3)	0.937	1.756	1.403	1.484	1.292
Dielectric constant (ε)	2.550	2.524	2.669	2.641	2.541
Reflection losses, R (%)	5.284	5.175	5.793	5.669	5.243