Journal of Luminescence 146 (2014) 358–363

Contents lists available at ScienceDirect

Journal of Luminescence

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

Luminescence studies of Dy^{3+} doped bismuth zinc borate glasses

B. Shanmugavelu, V.V. Ravi Kanth Kumar *

Department of Physics, Pondicherry University, Puducherry-605 014, India

ARTICLE INFO

Article history:
Received 4 June 2013
Received in revised form
4 October 2013
Accepted 5 October 2013
Available online 12 October 2013

Keywords:
Borate glasses
Judd–Ofelt analysis
Luminescence
Radiative properties
White light
Lifetime

ABSTRACT

Glasses having composition of $(100-x)$ $(1Bi_2O_3–1ZnO–1B_2O_3)$-xDy_2O_3 (where x=0.1, 0.3, 0.5, 1 and 2 mol%) were prepared by melt quenching method and characterized through optical absorption, emission and decay curve measurements. Optical absorption spectra have been analyzed using Judd–Ofelt theory. Asymmetric ratio, the intensity ratio of yellow to blue transitions, has been calculated from the emission spectra to understand the symmetry around the Dy^{3+} ions in the glass matrix. The emission spectra have been analyzed in the framework of CIE 1931 chromaticity colour coordinates in order to find out the white light emission characteristics of the glasses. The decay curve measurements exhibit single exponential behaviour up to 1 mol% of Dy^{3+} ions whereas non exponential behaviour is observed for 2 mol% of Dy^{3+} ions. The non exponential curve has been fitted to the Inokuti–Hirayama model to understand the nature of energy transfer process.

1. Introduction

Rare earth doped glasses have received much attention due to their potential applications as solid state laser materials, optical amplifiers, solar concentrators and light emitting diodes [1–4]. Currently a lot of importance is given for the generation of white light in the glasses by incorporating rare earth ions and transition metal ions [5–8]. Among various rare earth ions Dy^{3+} ion have attracted many researchers because of its capability to produce white light even as a single ion. Hence, studies on optical properties of Dy^{3+} doped glasses have gained significance [9–13]. Apart from the white light application, Dy^{3+} doped glasses are extensively studied for its 1.3 μm emission that can be utilized for optical amplification in the near infra red region [14–16]. The Dy^{3+} doped glasses are also used in the emission of laser radiation at 3 μm in the mid infrared region [17,18].

On the other hand, heavy metal oxide based glasses possess large transparency, high refractive index, high thermal and chemical stability. Bismuth borate based glasses are important materials for optical and optoelectronics applications. These glasses have been extensively studied for their nonlinear optical properties due to their large third order optical nonlinearity [19–21]. These glasses are also used as a good laser host materials due to its low phonon energy [22]. Moreover, the higher refractive index of bismuth borate based glasses facilitates the efficient radiative transitions in rare earth doped systems. Many studies on bismuth borate glasses with rare earth doping have been carried out in order to find out the applicability of these glasses as optical amplifier and laser host materials [23,24]. Recently, Dy^{3+} doped bismuth borate based glasses have been studied for its applicability as white light emitting diodes [25–26]. Earlier, we reported the detailed thermal properties of the transparent $Bi_2ZnOB_2O_6$ glass and optical properties of Dy^{3+} doped transparent $Bi_2ZnOB_2O_6$ glass/glass ceramics [27,28]. In continuation of our earlier work, in the present task we studied the effect of Dy^{3+} concentration in the $(1Bi_2O_3–1ZnO–1B_2O_3)$ (BZB) glass.

2. Experimental

The glasses having composition of $(100-x)$ $(1Bi_2O_3–1ZnO–1B_2O_3)$-xDy_2O_3 (where x=0.1, 0.3, 0.5, 1 and 2 mol% and labeled as BZBDy01, BZBDy03, BZBDy05, BZBDy1 and BZBDy2, respectively) were prepared by melt quenching method. Analar grade chemicals of Bi_2O_3, ZnO, H_3BO_3 and Dy_2O_3 obtained from M/s. Himedia, India were used as raw materials to prepare the glasses. The appropriate raw materials were melted at 1000 °C in a platinum crucible for about 45 min. The melt was swirled frequently to ensure homogeneity. The homogeneous melt was poured on a stainless plate and immediately it was pressed with another stainless plate. The prepared glasses were annealed in order to remove the thermal stress. The glasses were then ground and finally polished to a thickness of 1 mm to make them suitable for optical measurements. Density of the glasses was measured using water as an immersion liquid by Archimedes principle.

* Corresponding author. Tel.: +91 413 2654406; fax: +91 413 2655368.
E-mail addresses: ravi.phy@pondiuni.edu.in, vv_ravikanth@yahoo.com (V.V.R.K. Kumar).

0022-2313/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jlumin.2013.10.018

Refractive index of the glasses has been measured by Brewster angle method using a He–Ne laser (λ=632.8 nm). The absorption spectra were recorded using UV–Vis–NIR spectrophotometer (Carry 5000). The excitation and emission spectra were recorded at room temperature with 450-W Xenon CW lamp source and decay measurements were carried out with 75-W Xenon pulsed lamp source at 50 ms time per flash and 5 sample window using Fluorolog Spectrofluorometer (HORIBA Jobin Yvon).

3. Results and discussion

3.1. Absorption spectra and Judd–Ofelt (J–O) analysis

The Vis-NIR absorption spectra of the Dy^{3+} doped BZB glasses are shown in Fig. 1. The absorption spectra consist of eight bands that are located at 452, 473, 754, 803, 902, 1094, 1277 and 1685 nm, and are assigned to $^6H_{15/2}$ to $^4I_{15/2}$, $^4F_{9/2}$, $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}+{}^6H_{7/2}$, $^6F_{11/2}+{}^6H_{9/2}$ and $^6H_{11/2}$ transitions, respectively. The intensities of the absorption bands are usually expressed in terms of oscillator strength. The experimental oscillator strength of an absorption band (f_{exp}) can be determined by measuring the integrated areas under the absorption bands from the absorption spectrum through the following expression [29]

$$f_{exp} = \frac{2.303mc^2}{N\pi e^2}\int \varepsilon(\upsilon)d\upsilon = 4.32\times 10^{-9}\int \varepsilon(\upsilon)d\upsilon \quad (1)$$

where m and e are mass and charge of an electron, c is the velocity of light, N is the Avogadro's number, $\varepsilon(\upsilon)$ is the molar absorptivity of a band at wavenumber υ (cm^{-1}). The theoretical oscillator of an f–f transition can be evaluated using the J–O theory [30,31]. In this theory, the calculated oscillator strength of an induced electric-dipole transition from the ground state ΨJ to an excited state $\Psi' J'$ is given by

$$f_{cal} = \frac{8\pi^2 mc\upsilon}{3h(2J+1)}\frac{(n^2+1)^2}{9n}\sum_{\lambda=2,4,6}\Omega_\lambda(\Psi J||U^\lambda||\Psi' J')^2 \quad (2)$$

where n is refractive index of the medium, υ is the energy of the transition in cm^{-1} and h is the Plank's constant. J is the total angular momentum of the ground state, Ω_λ (λ=2, 4, 6) are J–O intensity parameters and $||U^\lambda||^2$are the doubly reduced matrix elements of the unit tensor operator evaluated from the intermediate coupling scheme for a transition ΨJ to $\Psi' J'$. The reduced matrix elements $||U^\lambda||^2$ (λ=2, 4, 6) were taken from literature [32]. A least square fit method is then applied to Eq. (2) to obtain a good fit between the experimental and calculated oscillator strengths as well as to obtain J–O intensity parameters (Ω_λ). The quality of the fit known as the root mean square deviation (σ_{rms}) between the f_{exp} and f_{cal} is given by

$$\sigma_{rms} = \sqrt{\frac{\sum_{i=1}^{N}(f_i^{exp}-f_i^{cal})^2}{N}} \quad (3)$$

where f_i^{exp} and f_i^{cal} are the experimental and calculated oscillator strengths, respectively, i and N refers total number of levels included in the fit.

The experimental and calculated oscillator strengths along with J–O parameters for all the samples are listed in Table 1. The obtained small root mean square value indicates that the quality of fit is good. The transition intensities are characterized by three sensitive parameters known as J–O intensity parameters, Ω_λ (λ=2, 4 and 6), which depend on the local environment. The relative magnitudes of Ω_λ are useful to explain the bonding, symmetry and stiffness of the host matrices [33]. The Ω_2 parameter indicates the covalence of the metal–ligand bond, whereas Ω_4 and Ω_6 related to the bulk properties such as viscosity and rigidity of the host matrix. In the present system, the value of Ω_2 is higher for BZBDy05 glass than other samples. This suggests that covalency

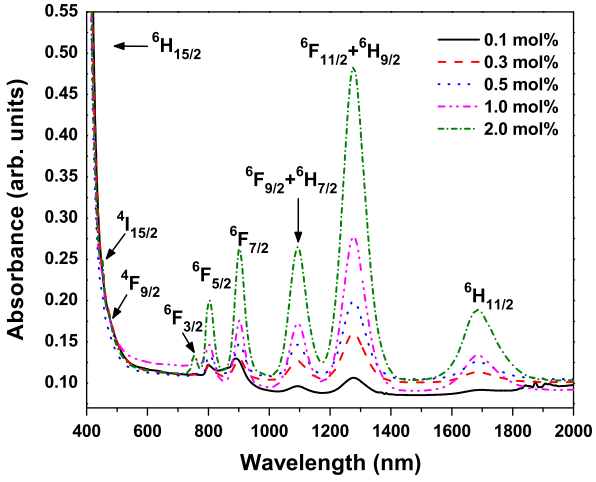

Fig. 1. Optical absorption spectra of the BZB glasses with different Dy^{3+} concentrations.

Table 1
Experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths, root mean square deviation (σ_{rms}), refractive index (n), density (d) (g/cm^3) and Judd–Ofelt parameters ($\Omega_\lambda \times 10^{-20}$ cm^2) for Dy^{3+} ions in BZB glasses.

Transition $^6H_{15/2}\rightarrow$	BZBDy01		BZBDy03		BZBDy05		BZBDy1		BZBDy2	
	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}
$^6H_{11/2}$	0.45	1.40	1.61	1.51	1.72	1.57	1.38	1.33	1.44	1.39
$^6H_{9/2}+{}^6F_{11/2}$	6.58	6.45	6.66	6.67	6.82	6.84	6.47	6.47	6.70	6.70
$^6F_{9/2}+{}^6H_{7/2}$	2.54	2.99	2.58	2.54	2.66	2.58	2.67	2.67	2.70	2.68
$^6F_{7/2}$	4.14	2.48	2.30	2.45	2.19	2.53	2.28	2.26	2.23	2.33
$^6F_{5/2}$	2.14	1.17	1.19	1.25	1.35	1.30	0.89	1.08	1.16	1.13
$^6F_{3/2}$	0.07	0.22	0.07	0.23	0.10	0.24	0.09	0.20	0.10	0.21
$^4F_{9/2}$	0.03	0.19	0.10	0.19	0.14	0.19	0.13	0.17	0.14	0.18
$^4I_{15/2}$	0.35	0.48	0.25	0.53	0.27	0.55	0.26	0.46	0.27	0.48
σ_{rms}		±0.78		±0.14		±0.18		±0.11		±0.09
d	6.7392		6.7286		6.7183		6.7079		6.6974	
n	2.14		2.14		2.14		2.14		2.14	
Ω_2		3.78		4.56		4.72		4.03		4.29
Ω_4		1.35		0.63		0.58		1.14		1.05
Ω_6		1.79		1.91		1.99		1.65		1.72