Journal of Luminescence 202 (2018) 168–175

Contents lists available at ScienceDirect

Journal of Luminescence

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

Blue-yellow emission adjustability with aluminium incorporation for cool to warm white light generation in dysprosium doped borate glasses

Simranpreet Kaur[a], Deepawali Arora[a], Sunil Kumar[b], Gurinderpal Singh[b], Shaweta Mohan[c], Puneet Kaur[d], Kriti[a], Puneet Kaur[a], D.P. Singh[a,*]

[a] Department of Physics, Guru Nanak Dev University, Amritsar 143005, India
[b] Department of Physics, Khalsa College, Amritsar 143005, India
[c] Department of Physics, BBK DAV College Amritsar 143005, India
[d] Department of Mathematics, Guru Nanak Dev University, Amritsar 143005, India

ARTICLE INFO

Keywords:
Energy transfer
Optical properties
Activators, warm White LED glasses

ABSTRACT

A series of white light emitting Dy^{3+} doped lead borate (DY) and lead alumino borate (DYA) glasses have been prepared by melt quench technique and are explored by XRD, FTIR, optical absorptions, fluorescence and density measurements. In this paper an effort has been made to compare the structural changes and luminescence efficiencies of prepared glasses by changing dysprosium oxide content and glass network environment by adding aluminium oxide. The XRD profile of all the glasses confirms their amorphous nature and FTIR study shows the presence of BO_3 and BO_4 groups. Incorporation of Al_2O_3 in the glass system is responsible for a strong effect on luminescence of the present glass system. There is a strong correlation between Dy^{3+} ions concentration and the host glass composition on the energy transfer mechanism. The decay curves deviate gradually from single exponential function at lower concentrations to non-exponential behavior at higher concentrations. The Inokutie Hirayama (IH) model for $S = 6$ fits well the non-exponential decay curves that indicate dipole-dipole type energy transfer between donor and acceptor ions. The calculated chromaticity coordinates lie in the white region of CIE 1931 chromaticity diagram and are in excellent proximity with the standard equal energy white illuminant (0.333, 0.333). Furthermore, the calculated correlated color temperature and the yellow to blue (Y/B) ratio of the synthesized photonic glasses may offer the possibility of tuning the white light by varying concentration and host environment which could be useful for various photonic based device applications.

1. Introduction

Rare earth ions are widely studied in various crystalline and glassy systems. They play an eminent role in the development of number of optoelectronic devices such as lasers, sensors, light converters, hole burning high density memories, optical fibres and amplifiers [1–3]. Glasses incorporated with rare earth ions have been developed as promising host materials for lasing phenomenon owing to their suppleness of shape, size, transparency and ease of fabrication over their crystalline competitors. Recently, white light emitting diodes (WLEDs) have gained a lot of attention as they are promising candidates in place of conventional incandescent and fluorescent lamps, due to their less energy consumption and environmental benefits. Rare earth doped white color luminescence glass systems have some assorted advantages such as consistent light emission, easy manufacture, cheap fabrication cost and high thermal stability. White light emitting glasses has formally been developed by Zhang et al. [4] in 1991 and have attracted a lot of interest in current years [5–7]. The visible luminescence of the Dy^{3+} ion comprises of two strong bands one in blue and the other in yellow regions corresponding to $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transitions respectively. At an appropriate yellow to blue Y/B intensity ratio, Dy^{3+} ions are known to radiate white light. So, the luminescent materials doped with Dy^{3+} ions are used as two-band or white light phosphors [8,9]. Liu et al. [5] reported that the CaO-B_2O_3-SiO_2 glass doped with Dy^{3+} ions shows chromaticity coordinates in the white light region. Using the melt-quenching technique, Dy^{3+}doped lead phosphate [6] and lithium borate [7] glasses are prepared and characterized for white LED applications. For the similar applications, Leow et al. [8] prepared and studied the optical properties of $BaB_2Si_2O_8$ phosphor glasses doped with Dy^{3+} ions which showed blue and green emissions in the Photoluminescence (PL) spectrum. The white-emitting $Sr_3Y(PO_4)_3$: Dy^{3+} doped phosphors have been synthesized by Seo et al. [9], its emission properties are tuned by varying the concentrations of Dy^{3+} ions from 2% to 18% mol.

* Corresponding author.
E-mail address: dpsinghdr@gmail.com (D.P. Singh).

https://doi.org/10.1016/j.jlumin.2018.05.034
Received 31 January 2017; Received in revised form 9 May 2018; Accepted 10 May 2018

Heavy metal oxide (HMOs). [10,11] based rare earth doped glass systems have high lasing potencies due to their large mass, low field strength and high polarizability. Borate glasses incorporated with heavy metal oxides have been known to give strong fluorescence in the visible spectral region which is used as electro-optic modulators, electro-optic switches, solid state laser materials and non-linear parametric converters [12,13]. Another significant feature of borate glasses is the modifications in its structural properties with the addition of modifiers or intermediates. The network of the borate glasses are formed by gathering of BO_3 triangles and BO_4 tetrahedra units to form well defined and stable borate groups such as diborate, triborate, tetraborate etc., that constitute the random three-dimensional network of these stable groups rather than there random distribution in the network. The B_2O_3 based glasses are well known for their large (even larger than crystals) photo induced second order non-linear optical effects owing to a strong effect on luminescent efficiencies of these glasses [14]. Many researchers reported concentration quenching of photoluminescence at large doping concentration (greater than 1.0 mol%) of Dy_2O_3 in the glasses or they selected only 1.0 mol% of Dy_2O_3 to study the glasses systems [15–18]. To crack this erratum, we in the present study employed co-dopant technique, which is used to overcome the quenching state and to enhance the sensitivity for dopant. The addition of a second modifier reagent enhances the emission intensity, creates disruption in the lattice, opens the network structure, weakens the bond strength, and lowers the viscosity of glass [19–21].

The present work focusses on the role of Dy_2O_3 in absence/presence of aluminium oxide by making comparative study of two glass systems Dy_2O_3–PbO–B_2O_3 (DY) and Dy_2O_3–Al_2O_3–PbO–B_2O_3(DYA). Also, the lasing properties have been discussed by absorption, photoluminescence, lifetime and CIE chromaticity color coordinates for different applications in solid state lighting field.

2. Experimental details

The detailed composition of various samples prepared for the present investigation has been tabulated below in Table 1

The raw materials dysprosium oxide (Dy_2O_3), lead oxide (PbO), boronoxide (B_2O_3) and aluminium oxide (Al_2O_3) in proper amounts are mixed and grinded finely to get a final batch of 15 g. The grinded mixture is further melted in silica crucible for 1 h in an electric furnace at a temperature of 1200^0 C in normal atmosphere till the formation of a bubble free liquid. Further, the melt has been quenched into preheated steel mould and annealed at a temperature of 400^0C. It is allowed to cool to room temperature to eliminate thermal and mechanical stress. The obtained samples are then grounded using different grade of SiC and polished with cerium oxide to have maximum flatness making them amenable for spectroscopic studies.

3. Characterisation

To confirm the amorphous/crystalline nature of the samples, X-ray diffraction (XRD) study has been done using XRD- 7000 Shimadzu X-ray Diffractometer (Cu Kα, λ = 1.54434 Å) at the rate of 2°/min with 2θ varying from 10° to 70°. The standard Archimede's principle is used to find the density of glass samples by using a sensitive microbalance with pure benzene as the immersion fluid.

$$D = [W_A/(W_A - W_B)]d, \quad (1)$$

where W_A is the weight of sample in air, W_B is the weight of the sample in benzene, and d is the density of the benzene. The molar volume (V_{im}) is calculated with the help of following formula:

$$V_{im} = \Sigma x_i M_i/d \quad (2)$$

where x_i is the molar fraction of the component and M_i is its molecular weight. The optical absorption spectra of the polished samples has been recorded at room temperature with the help of a (UV–Vis–NIR) Perkin Elmer Lambda 35 Spectrometer in the range 200–1100 nm with a spectral resolution of ± 1 nm. The optical band gap (E_g) has been calculated using the model proposed by Mott and Davis for indirect transitions observed in case of glasses due to long range geometrical disorder. The fluorescence spectra of prepared samples has been recorded with the help of Perkin-Elmer Fluorescence LS 45 Spectrophotometer with a resolution of ± 1.0 nm. The time-resolved fluorescence spectra have been recorded with a BH-CHRONOS time resolved fluorescence spectrophotometer using laser diodes at an excitation wavelength of 386 nm. The infrared transmission spectra of the samples are measured by using Varian 660-IR FTIR Spectrophotometer with spectral resolution of 4 cm^{-1} in the wavenumber range 400–4000 cm^{-1}. The fine powder of prepared glasses is mixed with KBr in the ratio 1:100 (glass powder: KBr) and a pressure of 1.470×10^7 Pa is applied to the mixture to get homogenous pellets. The IR transmission measurements are made instantly after preparing the pellets to avoid moisture.

Table 1
Nominal chemical composition of prepared glasses samples (mole %).

Sample Code	xDy_2O_3–20PbO–(80-x)B_2O_3 and xDy_2O_3–(10-x) Al_2O_3–20PbO–70B_2O_3			
	Dy_2O_3 (%)	Al_2O_3(%)	PbO (%)	B_2O_3 (%)
DY1	0.5	0	20	79.5
DY2	1.0	0	20	79
DY3	1.5	0	20	78.5
DY4	2.0	0	20	78
DYA1	0.5	9.5	20	70
DYA2	1.0	9.0	20	70
DYA3	1.5	8.5	20	70
DYA4	2.0	8.0	20	70

4. Experimental results and discussion

4.1. X-ray diffraction analysis

X-ray diffraction patterns of DY and DYA glass samples (Fig. 1) confirms absence of continuous or discrete sharp peaks but consist of diffused halos that reflects the glassy nature of the prepared samples. However, the diffractograms associated with alumino borates show a slight hint of crystallinity with very low intensity broad and diffused peaks [22].

4.2. FTIR spectra of Dy_2O_3–PbO – B_2O_3 glasses and Dy_2O_3–Al_2O_3 – PbO – B_2O_3 glasses

4.2.1. Dy_2O_3–PbO – B_2O_3 glasses

The FTIR spectra of the prepared glass samples have been recorded at room temperature is shown Fig. 2(a & b) depicting the presence of

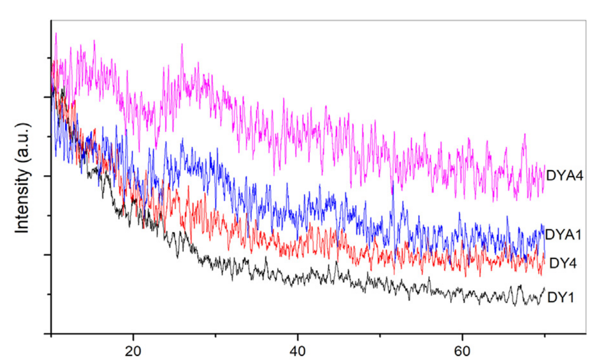

Fig. 1. XRD of DY and DYA prepared glass samples.