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Visible fluorescence characteristics of Dy^{3+} doped zinc alumino bismuth borate glasses for optoelectronic devices

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Abstract

Zinc Alumino Bismuth borate (ZnAlBiB) optical glasses of different compositions doped with 1 mol% of Dy^{3+} ions were prepared by the conventional melt quenching technique and investigated by the XRD, optical absorption, photoluminescence and decay curve analysis. The glassy nature of ZnAlBiB host has been confirmed through XRD measurements. From the absorption spectral measurements, the three phenomenological intensity parameters Ω_λ ($\lambda=2,4$ and 6) have been determined from the Judd–Ofelt (J–O) theory. By using JO intensity parameters, several radiative properties such as transition probability (A_R), branching ratio (β_R) and radiative lifetimes (τ_R) have been determined. The room temperature photoluminescence spectra of Dy^{3+} ions doped ZnAlBiB glasses gave two relatively intense emission bands $^4F_{9/2}\rightarrow{}^6H_{15/2}$ (blue), $^4F_{9/2}\rightarrow{}^6H_{13/2}$ (yellow) along with one faint band. The higher values of branching ratios and stimulated emission cross-sections for the $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition suggest the utility of these glasses as potential laser materials. The decay curves have been recorded for all the ZnAlBiB glasses to measure the quantum efficiency of these glasses by measuring the experimental lifetime (τ_{exp}). The radiative properties and CIE chromaticity co-ordinates have been evaluated from the emission spectra to understand the feasibility of these glasses for optoelectronic devices.

Keywords: Glasses; Rare-earths; Judd–Ofelt theory; Fluorescence properties

1. Introduction

Research towards the development of optical glasses has revolutionized the electronic and telecommunication industries. Several glass matrices such as fluorides, phosphates, borates, fluorophosphates, flouroborates etc. have been investigated to understand the effect of host glass on the lasing potentialities of the doped rare earth ions [1–5]. Spectroscopic investigation of rare earth ions doped glasses is of great importance due to their potential applications in developing lasers, optical fibers, infrared to visible up converters and phosphors. Design and development of an optical amorphous material needs the detailed characterization of fluorescence properties such as quantum efficiencies and lifetimes which in turn depends on the nature and type of the local environment around rare earth ion and on the phonon energies of the host matrix.

B_2O_3 is one of the best known glass formers with less scientific importance due to their high phonon energies [6]. Phonon energies have been reduced considerably by adding certain heavy metal oxides to give high quantum efficiencies. Hence, we have prepared a glass with the chemical constituents B_2O_3, ZnO, Al_2O_3 and Bi_2O_3. Among the rare earth ions, the Dy^{3+} activated luminescent materials have attracted much attention because of their significant applications as potential single phase white phosphors [7–10]. The Dy^{3+} ions show line like more intense absorption bands in the near infrared region and emissions at bright blue and yellow regions corresponding to $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transitions respectively along with feeble red emission corresponding to $^4F_{9/2}\rightarrow{}^6H_{11/2}$ transitions in visible region. White light emission from these glasses is possible by adjusting the yellow to blue intensity ratio.

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The lasing action of Dy^{3+} in visible region also finds a wide range of technological applications in commercial display sensors and for fiber optic amplification [11].

In the present work, Dy^{3+} doped heavy metal oxide glasses with Bi_2O_3, ZnO, and Al_2O_3 along with B_2O_3 were prepared by changing the molar ratio of the chemical composition to find out a suitable glass composition for lasing action. The present study mainly includes absorption, emission and life-time measurements of Dy^{3+} ions in the prepared glasses to select the efficient host material for solid state laser devices. From the absorption, emission and decay curve measurements various spectral properties such as oscillator strengths, JO intensity parameters, emission cross-sections, branching ratio's, lifetimes and quantum efficiencies are estimated for the excited $^4F_{9/2}$ emission levels of Dy^{3+} ions in these glasses by using the Judd–Ofelt theory. The color coordinates are also calculated to understand the utility of these glasses for white light emission.

2. Experimental

A series of Zinc Alumino Bismuth Borate Glasses (ZnAlBiB) doped with Dy^{3+} were prepared according to the chemical composition 60 B_2O_3 +9 ZnO+ (30−x) Al_2O_3 +x Bi_2O_3+1 Dy_2O_3 (x=5,10,15 and 20). For convenience the samples were designated as glass A to D in accordance with the 'x' value. Mixed batches were placed in high purity alumina crucibles and melted at 1200 °C for 20–30 min until bubble free liquid is formed in an electric furnace. The melt was then poured onto a pre-heated brass mold at 400 °C and are kept for annealing at room temperature to cool down at the rate of 10 °C/h to remove internal stresses. The glasses were cut and well-polished for optical measurements. Glass samples with excellent optical quality were obtained and densities were measured for all the glasses using the Archimedes principle with water as an immersion liquid. Refractive indices for the prepared glasses were measured using Brewster's law with a laser source of wavelength 650 nm. The optical absorption spectra of the samples were recorded at room temperature in the spectral wavelength range covering 750–1950 nm with a spectral resolution of 0.1 nm using Jasco model V-670 UV–vis–NIR spectrophotometer. The luminescence spectra and lifetime measurements were carried out at room temperature using JOBIN YVON Fluorolog-3 spectrofluorimeter with Xenon arc lamp as radiation source.

3. Results and discussion

3.1. XRD phase analysis

To confirm the glassy nature of the prepared glasses, an XRD spectrum was recorded for an undoped glass. Fig. 1 shows the XRD spectrum of undoped ZnAlBiB glass. The XRD pattern reveals no distinguishable intensity peaks, but shows a broad diffusion at low scattering angle which indicates the glassy nature of the system.

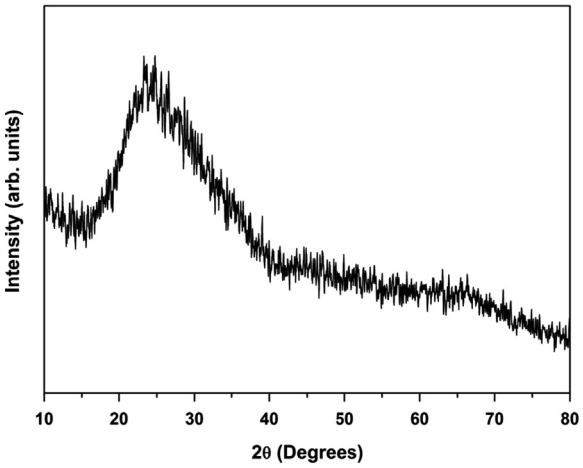

Fig. 1. XRD spectrum for ZnAlBiB glass.

Table 1
Various physical Parameters of Dy^{3+}-doped ZnAlBiB glasses.

Physical properties	Glass A	Glass B	Glass C	Glass D
Refractive index (n_d)	1.80	1.80	1.81	1.81
Density	3.54	3.79	4.04	4.29
Average molecular weight (gms)	101.36	119.56	137.76	155.96
Dy^{3+} ion concentration ($\times 10^{22}$ ions/cm^3)	2.11	1.91	1.77	1.66
Mean atomic volume (g/cm^3/atom)	6.49	7.16	7.75	8.26
Optical dielectric constant	2.25	2.25	2.27	2.28
Dielectric constant	3.25	3.25	3.27	3.28
Reflection losses (%)	8.19	8.22	8.28	8.31
Molar refraction	12.23	13.51	14.67	15.69
Polaron radius (Å)	1.74	1.73	1.84	1.88
Interatomic distance (Å)	3.68	3.80	3.91	3.99
Molecular electronic polarizability ($\times 10^{-23}$)	0.49	0.54	0.58	0.62
Field strength ($\times 10^{15}$)	9.97	9.34	8.87	8.50
Optical basicity	0.44	0.44	0.44	0.44

3.2. Physical properties

Various physical properties for the prepared glasses were determined using the expressions given in our previous paper [12] and are presented in Table 1. The optical basicity values which indicate the ability of a glass to donate negative charges to the probe ion were calculated for the present glassy system using the expression given by Duffy and Ingram [13].

3.3. Absorption spectral measurements

Optical absorption spectra have been measured for all the ZnAlBiB glasses in NIR region. Fig. 2 shows the NIR absorption spectrum for Glass A recorded at room temperature in the wavelength range 750–1950 nm. Each spectrum has same resemblance in absorption features with slight difference in intensities of various absorption bands and hence the spectra for remaining glasses were not shown in the manuscript. Each

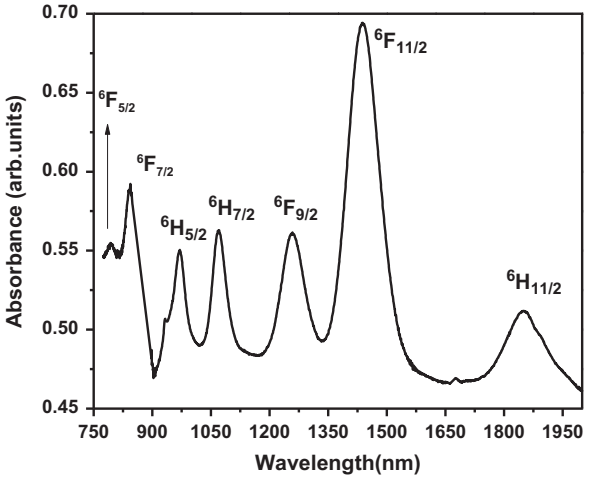

Fig. 2. NIR Absorption spectrum of Dy^{3+} ions in GlassA.

Table 2
Experimental ($f_{exp} \times 10^{-6}$) and calculated ($f_{cal} \times 10^{-6}$) oscillator strengths for Dy^{3+} doped ZnAlBiB glasses.

Transition $^4I_{9/2} \rightarrow$	Glass A		Glass B		Glass C		Glass D	
	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}
$^6H_{11/2}$	0.99	1.23	1.48	1.39	1.29	1.35	1.73	1.85
$^6F_{11/2}$	6.55	6.51	7.02	7.03	7.97	7.96	11.6	11.58
$^6F_{9/2}$	2.27	2.37	1.91	1.95	2.50	2.55	3.16	3.15
$^6H_{7/2}$	2.25	1.87	2.15	1.88	2.19	1.95	2.36	2.48
$^6H_{5/2}$	1.01	0.86	0.09	0.95	0.49	0.88	1.62	1.13
$^6F_{7/2}$	0.87	0.18	0.73	0.19	1.53	0.18	1.21	0.23
$^6F_{5/2}$	0.08	0.01	0.07	0.01	0.29	0.01	0.19	0.10
δ_{rms} ($\times 10^{-6}$)	± 0.323		± 0.399		± 0.551		± 0.425	

absorption spectrum consists of 7 absorption bands corresponding to the transitions $^6H_{15/2} \rightarrow {}^6F_{5/2}$, $^6F_{7/2}$, $^6H_{5/2}$, $^6H_{7/2}$, $^6F_{9/2}$, $^6F_{11/2}$ and $^6H_{11/2}$. The strong absorption of the host glass in UV region has resulted in the disappearance of some of the absorption bands in that region. To determine the JO intensity parameters for these glasses, all the seven absorption bands observed in the NIR region are used. Experimental oscillator strength (f_{exp}), which is a measure of intensity of absorption transition in a given matrix, has been determined from the area under the absorption curves using the formula given in the literature [14,15]. Table 2 represents the experimental and calculated oscillator strengths for ZnAlBiB glasses with small rms deviation which indicates the good fit between the two values and also supports the validity of Judd–Ofelt theory. The Judd–Ofelt intensity parameters given in Table 3 were calculated using the experimental values of oscillator strengths (f_{exp}) and the reduced matrix elements by least square fit method. The trend in JO intensity parameters in the present glasses are given in Table 3 along with the values reported for other glasses [16–20]. The JO intensity parameters are important to investigate the local structure and bonding in the vicinity of RE ions. According to Jorgensen and Resifeld [21], the magnitude of the Ω_2 parameter depends on the

Table 3
Comparison of JO parameters ($\Omega_\lambda \times 10^{-20}$ cm^2), spectroscopic quality factor ($\chi = \Omega_4/\Omega_6$) and their trend for Dy^{3+} doped ZnAlBiB glasses with different hosts.

System	Ω_2	Ω_4	Ω_6	χ (Ω_4/Ω_6)	Trend	Reference
Glass A	6.2	1.73	2.1	0.82	$\Omega_2 > \Omega_6 > \Omega_4$	Present work
Glass B	7.78	0.64	2.32	0.28	$\Omega_2 > \Omega_6 > \Omega_4$	Present work
Glass C	7.8	2.02	2.14	0.94	$\Omega_2 > \Omega_6 > \Omega_4$	Present work
Glass D	12.03	2.33	2.74	0.85	$\Omega_2 > \Omega_6 > \Omega_4$	Present work
$LiNbO_3$	5.42	1.14	2.51	0.45	$\Omega_2 > \Omega_6 > \Omega_4$	[16]
Phosphate	5.5	1.31	1.88	0.7	$\Omega_2 > \Omega_4 > \Omega_6$	[17]
NaTFP	5.53	2.13	0.88	2.42	$\Omega_2 > \Omega_4 > \Omega_6$	[18]
LiTFP	7.06	2.2	0.97	2.27	$\Omega_2 > \Omega_4 > \Omega_6$	[18]
Lead Borate	4.9	0.94	2.07	0.45	$\Omega_2 > \Omega_6 > \Omega_4$	[19]
CFBDy10	5.98	2.33	2.33	1	$\Omega_2 > \Omega_4 = \Omega_6$	[20]

covalency of metal–ligand bond and also on the asymmetry of ion sites in the neighborhood of RE ion. On the other hand the magnitudes of Ω_4 and Ω_6 parameters are related to the bulk properties such as viscosity and rigidity of the medium in which the ions are situated. The largest magnitude of Ω_2 observed for all ZnAlBiB glasses suggests that, the bonding of Dy^{3+} ions with the ligands is of covalent nature and the rare earth ion sites are having lower asymmetry in these host glasses.

Due to the inhomogeneity of host around the rare-earth ions, certain absorption transitions of rare earth ion are very sensitive to the host environment and ion concentration [22]. Such transitions are known as hypersensitive transitions obeying the selection rules $\Delta S = 0$ $\Delta L \leq 2$ and $\Delta J \leq 2$ [23]. The hypersensitive transitions are associated with the large values of oscillator strengths as well as reduced matrix element $\|U^\lambda\|$. As seen from Table 2, the hypersensitive transition $^6H_{15/2} \rightarrow {}^6F_{11/2}$ possessing maximum value of oscillator strengths (f_{exp}) which is solely dependent on the Ω_2 value and also sensitive to the local symmetry of ligand field or covalent bond of Dy^{3+} ion [23].

The spectroscopic quality factor (Ω_4/Ω_6), which is used to characterize the stimulated emission in a host matrix is also given in Table 3. The value of spectroscopic quality factor (Ω_4/Ω_6) allows us to predict the channels by which the rare-earth ions from the metastable state $^4F_{9/2}$ can relax through luminescence [24]. The values of (Ω_4/Ω_6) for the present glasses are in consistent with the values reported for the others glasses doped with Dy^{3+} ions [16–20]. The reasonably high value of spectroscopic quality factor (Ω_4/Ω_6) predicts efficient stimulated emission in the present host glasses.

3.4. Radiative properties and Luminescent analysis

The J–O parameters evaluated from least square fit are used to predict the radiative properties such as radiative transition probability (A_R), total transition probability (A_T), radiative lifetime (τ_R) and branching ratio (β_R) for the electric dipole transitions between an excited level to its lower lying levels.

The radiative transition probability A_R can be expressed as

$$A_R = \frac{64\pi^4 e^2 \vartheta^3}{3h(2J+1)}\left[\frac{n(n^2+2)^2}{9}S_{ed} + n^3 S_{md}\right] \quad (1)$$

The sum of radiative transition probability from a particular energy level to all the lower levels gives total radiative transition probability A_T.

$$A_T = \sum A_R \quad (2)$$

The radiative lifetime (τ_R) of an excited state is determined by using the formula

$$\tau_R = \frac{1}{A_T} \quad (3)$$

The fluorescence branching ratio (β_R) is another important parameter in understanding the optical potentiality of the prepared glass material, which characterizes the possibility of attaining stimulated emission for a specific transition and can be determined by

$$\beta_R = \frac{A_R}{A_T} \quad (4)$$

The peak stimulated emission cross-section σ_e (ΨJ, $\Psi J'$) between the states ΨJ and $\Psi J'$ having the transition probability of $A_R(\Psi J, \Psi J')$ can be calculated by

$$\sigma_{se}(\Psi J\ ,\ \Psi J') = \frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_p} A_R(\Psi J\ ,\ \Psi J') \quad (5)$$

where λ_p is the peak wavelength of emission and $\Delta\lambda_p$ is the effective line width found by dividing the area of the emission band by its average height. The quantum efficiency (η) is defined as the ratio of the number of photons emitted to the number of photons absorbed. For RE ion system, it is equal to the ratio of the measured lifetime (τ_{mes}) to the calculated radiative lifetime (τ_R) [18].

$$\eta = \frac{\tau_{mes}}{\tau_R} \quad (6)$$

The radiative lifetime (τ_R) is calculated from the JO theory whereas the measured lifetimes (τ_{mes}) of the emission transition is measured by recording the decay curves and by taking first e-folding times the decay curves.

To analyze the luminescence properties of the prepared glasses, it is necessary to know the correct excitation wavelength of the Dy^{3+} ions. For this purpose we have recorded the excitation spectrum for all the glasses by monitoring emission at 484 nm and are shown in Fig. 3. Totally four excitation bands are observed in all the glasses at wavelengths approximately 350, 365, 387 and 426 nm corresponding to $^6H_{15/2} \rightarrow {}^6P_{7/2}$, $^4P_{3/2}$, $^4I_{13/2}$ and $^4G_{11/2}$ transitions respectively. Among all the excitation bands, a band corresponding to $^6H_{15/2} \rightarrow {}^4I_{13/2}$ (387 nm) is more intense and is used as an excitation wavelength to record the emission spectra for all the glasses. Fig. 4 shows the emission spectra of 1.0 mol % of Dy^{3+} ions in ZnAlBiB glasses recorded with an excitation wavelength of 387 nm. The emission spectra contains two intense emission bands approximately at 484 nm (blue) and 576 nm (yellow) corresponding to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions

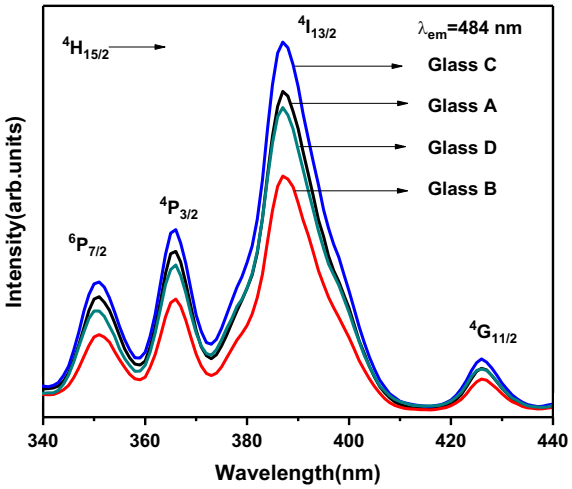

Fig. 3. Excitation spectra of Dy^{3+} ions in ZnAlBiB glasses.

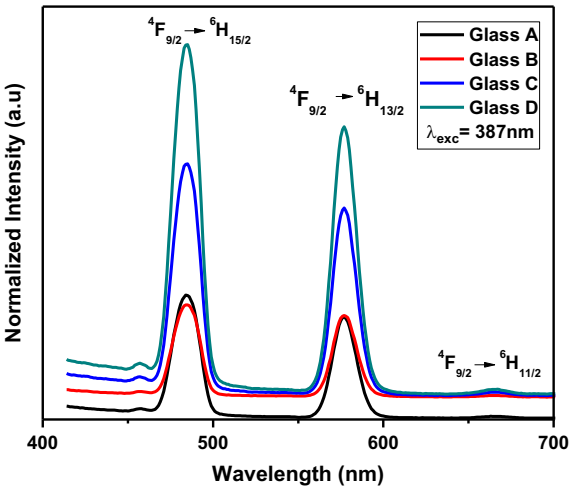

Fig. 4. Fluorescence spectra for Dy^{3+} ions in ZnAlBiB glasses.

respectively. In addition to these bands, one weak band corresponding to the transition $^4F_{9/2} \rightarrow {}^6H_{11/2}$ has also been observed. Among the two intense transitions, a transition corresponding to $^4F_{9/2} \rightarrow {}^6H_{13/2}$ is in yellow region and hypersensitive obeying the selection rules $\Delta J = \pm 2$ and $\Delta L = \pm 2$ [23]. When the Dy^{3+} ions are excited with 387 nm to the $^4I_{13/2}$, due to small energy gaps between all energy states lying above 21,000 cm^{-1}, the $^4F_{9/2}$ state is rapidly populated by non-radiative relaxation and as a result blue and yellow luminescence originating from the $^4F_{9/2}$ state is observed. The $^4F_{9/2}$ level possesses purely radiative relaxation rates since this level has sufficient energy gap ~8000 cm^{-1} with respect to the next lower level of $^6F_{5/2}$. The emission spectra of these glasses are similar to each other and are comparable with those obtained for other Dy^{3+} doped glass systems [25–27].

To understand the lasing potentialities of these glasses, the JO theory [14,15] has been applied to determine radiative

properties such as transition probability (A_R), total transition probability (A_T), fluorescence branching ratio (β_R), and stimulated emission cross section for the emission transitions $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ using the relevant expressions given above and are documented in Table 4. The fluorescence branching ratio which characterizes and makes the transition as potential for laser emission, if its value $\beta_R \geq 0.5$. In the present work, the emission transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$ has higher β_R than the other observed transition and is comparable to the values reported in literature [18,19]. The experimental branching ratios (β_{exp}) are obtained by using the relative intensities of individual peaks to that of the total intensity of emission peaks and are given in Table 4. The variation in radiative and experimental branching ratios may be attributed to the non-radiative contributions from the $^4F_{9/2}$ level of Dy^{3+} ions in these ZnAlBiB glasses.

The value of stimulated emission cross-section has been used to identify the potential laser transition of rare earth ions in glasses. The stimulated emission cross-sections of the order of $24.6–30.2 \times 10^{-22}$ cm^2 obtained for $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition in ZnAlBiB glasses are in good agreement with the values reported for the other glass hosts [18,19]. The relatively larger β_R and stimulated emission cross-sections observed for ZnAlBiB glasses makes them as promising materials for lasing action through the emission channel $^4F_{9/2} \rightarrow {}^6H_{13/2}$ with its wavelength around 578 nm. From Table 4, it is clear that among all the ZnAlBiB glasses, the glass B which possesses more β_R and σ_{se} values when compared with other glasses. Hence glass B can recommended as a good host for lasing emission at 578 nm. A glassy material doped with rare earth can act as good optical fiber, if the gain band width ($\sigma_{se} \times \Delta\lambda_P$) and optical gain ($\sigma_{se} \times 1/A_T$) parameters are having higher values. The relatively higher values of ($\sigma_{se} \times \Delta\lambda_P$) and ($\sigma_{se} \times 1/A_T$) obtained for ZnAlBiB glasses suggests that they are suitable candidates for optical amplification.

Table 4
Emission peak wavelength (λ_P)(nm), effective band widths($\Delta\lambda_P$)(nm), radiative properties such as Transition probability (A_R)(s^{-1}), total radiative transition probabilities(A_T) (s^{-1}), experimental and calculated branching ratios (β_{exp} and β_R) and stimulated emission cross- sections (σ_{se})($\times 10^{-22}$ cm^2) for Intense emission transitions of Dy^{3+} doped ZnAlBiB glasses.

Transition $^4F_{9/2} \rightarrow$	parameter	Glass A	Glass B	Glass C	Glass D
$^6H_{15/2}$	λ	485.00	485.00	485.00	485.00
	$\Delta\lambda_P$	16.50	16.50	15.25	16.50
	A_R	166.18	191.26	168.38	195.60
	A_T	1458.00	1667.00	1402.00	1817.00
	β_{exp}	0.57	0.55	0.59	0.62
	β_R	0.11	0.12	0.12	0.11
	σ_{se}	2.29	2.63	2.52	2.33
$^6H_{13/2}$	λ	576.80	576.80	576.80	576.80
	$\Delta\lambda_P$	15.25	16.50	16.50	16.50
	A_R	923.35	1096.40	889.15	1207.28
	A_T	1458.00	1667.00	1402.00	1817.00
	β_{exp}	0.50	0.57	0.42	0.38
	β_R	0.63	0.66	0.64	0.66
	σ_{se}	28.00	30.20	24.60	24.80

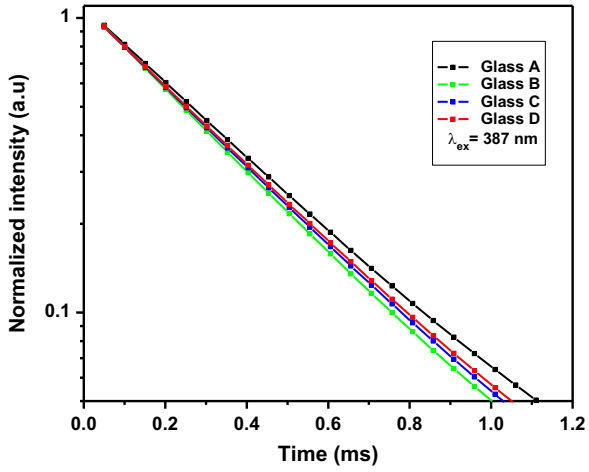

Fig. 5. Logarithmic plot of the decay curve of $^4F_{9/2}$ state of 1 mol% of Dy^{3+} in various ZnAlBiB glasses.

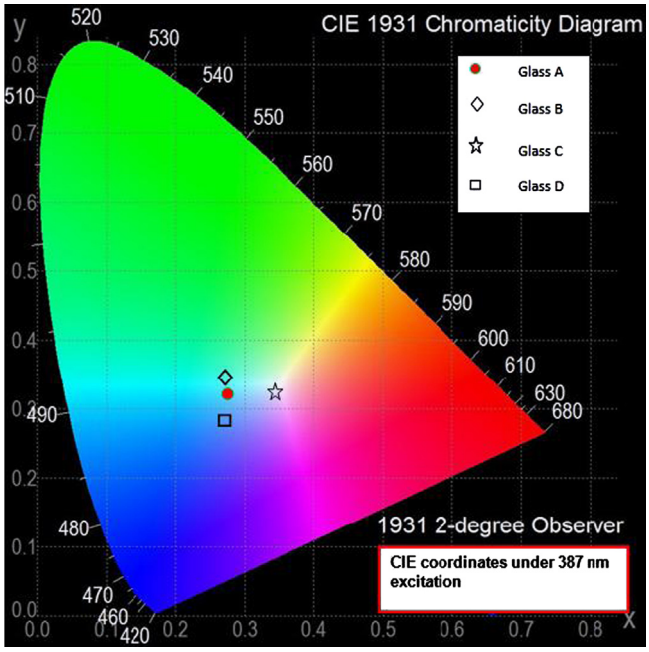

Fig. 6. CIE chromaticity diagram for ZnAlBiB glasses under 387 nm.

3.5. Fluorescence decay analysis

The luminescence decay curves originating from the $^4F_{9/2}$ level of Dy^{3+} ions in the ZnAlBiB glasses were measured with an excitation wavelength of 387 nm and are shown in Fig. 5. All the decay curves are single exponential in nature. The measured lifetimes (τ_{exp}) of excited $^4F_{9/2}$ fluorescent level has been determined by taking first e-folding times the decay curves. The measured lifetimes (τ_{exp}) are found to be 331, 302, 315 and 320 μs for glass A, B, C and D respectively. Among all ZnAlBiB glasses, glass A has got highest measured lifetime. The measured lifetimes observed for ZnAlBiB glasses are found to be higher in magnitude than those of 1.0 mol% Dy^{3+} ions doped different hosts [28–31]. The radiative

lifetimes (τ_R) of $^4F_{9/2}$ excited level obtained from JO theory for glass A, B, C and D are 685, 599, 712 and 709 μs respectively. The considerable discrepancy between the radiative (τ_R) and measured (τ_{exp}) lifetimes of $^4F_{9/2}$ level indicates that there should be some non-radiative decay contributions. Since, the decay curves are single exponential, the non-radiative decay rates (W_{NR}) are equal to the multi phonon relaxation rates (W_{MPR}) only.

If the experimentally measured lifetime of the emitting state is denoted by τ_{exp}, the total decay rate ($1/\tau_{exp}$) is the sum of radiative (A_R) and non-radiative (W_{NR}) decay rates.

$$(1/\tau exp) = (A_T) + (W_{NR}) \quad (7)$$

Therefore the non-radiative relaxation rate $W_{NR}=(1/\tau_{exp})-(1/\tau_R)$. The non-radiative relaxation rates calculated for glasses A, B, C and D are 1561, 1641, 1770 and 1714 s^{-1} respectively. The measured lifetimes (τ_{exp}), radiative lifetimes (τ_R), quantum efficiency (η) and non-radiative relaxation rates evaluated for Dy^{3+} doped ZnAlBiB glasses are given in Table 5. It has been observed that glass B possesses more quantum efficiency than the other glasses. Similar trend has been observed for β_R and σ_{se} values in glass B than the other glasses. Hence, glass B could be opted as a good lasing material in the visible region at 576 nm.

3.6. CIE chromaticity coordinates

The CIE color coordinates for Dy^{3+} doped ZnAlBiB glasses were calculated from the emission spectra and are given in Table 6 along with the Y/B ratio. The Y/B ratio for all the Dy^{3+} doped ZnAlBiB glasses are approximately same and equal to 1.19. The high values of Y/B for the present glasses indicates high degree of covalence between Dy^{3+} and oxygen ions [19]. The Y/B intensity ratios of visible emission indicate the feasibility of generating white light in the Dy^{3+} doped ZnAlBiB glasses. Fig. 6 shows the CIE chromaticity diagram for ZnAlBiB glasses. It has been observed that the chromaticity coordinates for ZnAlBiB glasses doped with Dy^{3+} ions are located in the white light region. Hence, it is suggested that ZnAlBiB glass at different compositions are quite suitable for white light emission under 387 nm excitation. Among all the ZnAlBiB glasses, the glass C is possessing good chromaticity color coordinates ($x=0.34$, $y=0.32$), which are very close to the ideal white light emission color coordinates ($x=0.33$, $y=0.33$). The prominent excitation wavelength 387 nm in the present glasses match well with the excitation wavelengths of the commercial UV LEDs ($\lambda_{em}=\sim340$–410 nm). Hence, it is concluded that glass C could be a promising host glass for white LED under 387 nm excitation.

Table 5
Experimental lifetimes (τ_{exp})(μs), Radiative lifetimes (τ_R)(μs), quantum efficiency (η%) and non-radiative relaxation rate (W_{NR})(S^{-1}) for Dy^{3+} doped ZnAlBiB glasses.

Glass system	τ_{exp}	τ_R	η (%)	W_{NR}
Glass A	331	685	48	1561
Glass B	302	599	50	1641
Glass C	315	712	44	1770
Glass D	320	709	45	1714

Table 6
CIE Chromaticity color co-ordinates and yellow ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) to blue ($^4F_{9/2}\rightarrow{}^6H_{15/2}$) intensity ratios (Y/B) for the visible fluorescence spectra of Dy^{3+} doped ZnAlBiB glasses.

Glass system	Color co-ordinates	Y/B
Glass A	$x=0.28$, $y=0.32$	1.1919
Glass B	$x=0.27$, $y=0.35$	1.1917
Glass C	$x=0.34$, $y=0.32$	1.1919
Glass D	$x=0.27$, $y=0.29$	1.1919

4. Conclusions

Good optical quality Dy^{3+} doped ZnAlBiB glasses were prepared by the conventional melt quenching technique. The visible fluorescence characteristics of Dy^{3+} ions in these glasses for different compositions have been analyzed by using absorption, fluorescence and decay measurements to find the suitability of these materials for optoelectronic devices such as lasers and white LEDs. The absorption and fluorescent spectra of these glasses were analyzed by using J–O theory. Among all the glasses, Glass B possessing better radiative properties and quantum efficiencies. The magnitudes of evaluated CIE chromaticity co-ordinates from the emission spectra of Dy^{3+} ions in these glasses excited at 387 nm located in the white light region and confirms the possibility to generate white light emission from these glasses. Among all the glasses, the CIE chromaticity co-ordinates of Glass C are in good agreement with the ideal white color coordinates. Hence it can be concluded that Glass B and Glass C are promising optoelectronic devices for lasers and white LEDs under 387 nm, respectively.

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References

[1] Hai Lin, Edwin Yue-Bun Pun, Xiaojun Wang, Xingren Lin, Intense visible fluorescence and energy transfer in Dy^{3+}, Tb^{3+}, Sm^{3+} and Eu^{3+} doped rare-earth borate glasses, Journal of Alloys and Compounds 390 (2005) 197–201.

[2] M. Jayasimhadri, Kiwan Jang, Ho-Sueb Lee, Baojiu Chen, Soung SooYi, Jung-Hyun Jeong, White light generation from Dy^{3+}-doped ZnO–B_2O_3–P_2O_5 glasses, Journal of Applied Physics 106 (2009) 0131054.

[3] M. Jayasimhadri, L. Rama Moorthy, R.V.S.S.N. Ravi Kumar, An investigation of the optical properties of Nd^{3+} ions in alkali tellurofluorophosphate glasses, Optical Materials 29 (2007) 1321–1326.

[4] J. Pisarska, R. Lisiecki, W. Ryba-Romanowski, T. Goryczka, W.A. Pisarski, Unusual luminescence of Dy^{3+}-doped lead borate glass after heat treatment, Chemical Physics Letters 489 (2010) 198–201.
[5] Liyuan Xiao, Qin Xiao, Yingliang Liu, Pengfei Ai, Yidong Li, Houjin Wang, A transparent surface-crystallized Eu^{2+}, Dy^{3+} co-doped strontium aluminate long-lasting phosphorescent glass-ceramic, Journal of Alloys and Compounds 495 (2010) 72–75.
[6] S.M. Kaczmarek, $Li_2B_4O_7$ glasses doped with Cr, Co, Eu and Dy, Optical Materials 19 (2002) 189–194.
[7] R. Martínez-Martínez, A.C. Lira, A. Speghini, C. Falcony, U. Caldiño, Blue–yellow photoluminescence from $Ce^{3+} \rightarrow Dy^{3+}$ energy transfer in HfO_2:Ce^{3+}:Dy^{3+} films deposited by ultrasonic spray pyrolysis, Journal of Alloys and Compounds 509 (2011) 3160–3165.
[8] B.V. Ratnam, M. Jayasimhadri, Kiwan Jang, Ho Sueb Lee, Soung-Soo Yi, J.-H. Jeong, White light emission from $NaCaPO_4$:Dy^{3+} phosphor for UV-based white light emitting diodes, Journal of the American Ceramic Society 93 (2010) 3857–3861.
[9] Ying Fang, Weidong Zhuang, Yunsheng Hu, Xinyu Ye, Xiaowei Huang, Luminescent properties of Dy^{3+} ion in $Ca_8Mg(SiO_4)_4Cl_2$, Journal of Alloys and Compounds 455 (2008) 420–423.
[10] Xin-yuan Sun, Shi-ming Huang, Xiao-san Gong, Qing-chun Gao, Zi-piao Ye, Chun-yan Cao, Spectroscopic properties and simulation of white-light in Dy^{3+}- doped silicate glass, Journal of Non-Crystalline Solids 356 (2010) 98–101.
[11] D.P. Machewirth, K. Wei, V. Krasteva, R. Datta, E. Snitzer, G.H. Sigel Jr., Optical characterization of Pr^{3+} and Dy^{3+} doped chalcogenide glasses, Journal of Non-Crystalline Solids 213 (1997) 295–303.
[12] A. Srinivasa Rao, B. Rupa Venkateswara Rao, M.V.V.K.S. Prasad, J.V. Shanmukha Kumar, M. Jayasimhadri, J.L. Rao, R.P.S. Chakradhar, Spectroscopic and optical properties of Nd^{3+} doped fluorine containing alkali and alkaline earth zinc aluminophosphate optical glasses, Physica B: Condensed Matter 404 (2009) 3717 –372.
[13] J.A. Duffy, M.D. Ingram, Optical basicity-IV: influence of electronegativity on the Lewis basicity and solvent properties of molten oxyanion salts and glasses, Journal of Inorganic and Nuclear Chemistry 37 (1975) 1203–1206.
[14] B.R. Judd, Optical absorption intensities of rare-earth ions, Physical Review 127 (1962) 750–761.
[15] G.S. Ofelt, Intensities of crystal spectra of rare-earth ions, Journal of Chemical Physics 37 (1962) 511–520.
[16] G. Dominiak-Dzik, W. Ryba-Romanowski, M.N. Palatnikov, N.V. Sidorov, V.T. Kalinnikov, Dysprosium-doped $LiNbO_3$ crystal. Optical properties and effect of temperature on fluorescence dynamics, Journal of Molecular Structure 704 (2004) 139–144.
[17] R. Vázquez, M. Osellame, R. Marangoni, E. Ramponi, M Diéguez, M. Ferrari, Mattarelli,Optical properties of Dy3+ doped yttrium–aluminium borate, Journal of Physics: Condensed Matter 16 (2004) 465.
[18] M. Jayasimhadri, L.R. Moorthy, K. Kojima, K. Yamamoto, Noriko Wada, Noriyuki Wada, Optical properties of Dy^{3+} ions in alkali tellurofluorophosphate glasses for laser materials, Journal of Physics D: Applied Physics 39 (2006) 635–641.
[19] Joanna pisarska, Optical properties of lead borate glasses containing Dy^{3+} ions, Journal of Physics: Condensed Matter 21 (2009) 285101.
[20] J. Suresh Kumar, K. Pavani, A. Mohan Babu, Neeraj Kumar Giri, S.B. Rai, L. Rama Moorthy, Fluorescence characteristics of Dy^{3+} ions in calcium fluoroborate glasses, Journal of Luminescence 130 (2010) 1916–1923.
[21] C.K. Jorgensen, R. Reisfeld, Judd–Ofelt parameters and chemical bonding, Journal of the Less Common Metals 93 (1983) 107–112.
[22] C.K. Jorgensen, B.R. Judd, Hypersensitive pseudo-quadrupole transitions in lanthanides, Molecular Physics 8 (1964) 281–290.
[23] S. Tanabe, T. Ohyagi, N. Soga, T. Hanada, Compositional dependence of Judd–Ofelt parameters of Er^{3+} ions in alkali-metal borate glasses, Physical Review B 46 (1992) 3305–3310.
[24] Dhiraj K. Sardar, William M. Bradley, Raylon M. Yow, John B. Gruber, Bahram Zandi, Optical transitions and absorption intensities of $Dy^{3+}(4f^9)$ in YSGG laser host, Journal of Luminescence 106 (2004) 195–203.
[25] Zhiyong Yang, Wei Chen, Lan Luo, Dy^{3+}-doped Ge–Ga–Sb–Se glasses for 1.3 μm optical fiber amplifiers, Journal of Non-Crystalline Solids 351 (2005) 2513–2518.
[26] P. Babu, C.K. Jayasankar, Spectroscopic properties of Dy^{3+} ions in lithium borate and lithium fluoroborate glasses, Optical Materials 15 (2000) 65–79.
[27] C.K. Jayasankar, V. Venkatramu, S. Surendra Babu, P. Babu, Luminescence properties of Dy^{3+} ions in a variety of borate and fluoroborate glasses containing lithium, zinc and lead, Journal of Alloys and Compounds 374 (2004) 22–26.
[28] A. Mohan Babu, B.C. Jamalaiah, J. Suresh Kumar, T. Sasikala, L. Rama Moorthy, Spectroscopic and photoluminescence properties of Dy^{3+} -doped lead tungsten tellurite glasses for laser materials, Journal of Alloys and Compounds 509 (2011) 457–462.
[29] S.A. Saleem, B.C. Jamalaiah, M. Jayasimhadri, A. Srinivasa Rao, Kiwan Jang, L. RamaMoorthy, Luminescent studies of Dy^{3+} ion in alkali lead telluro fluoro borate glasses, Journal of Quantitative Spectroscopy and Radiative Transfer 112 (2011) 78–84.
[30] G.S. Raghuvanshi, H.D. Bist, H.C. Khandpal, Luminescence characteristics of Dy^{3+} in different host matrices, Journal of Physics and Chemistry of Solids 43 (1982) 781–783.
[31] M.V. Vijaya Kumar, B.C. Jamalaiah, K. Rama Gopal, R.R. Reddy, Optical absorption and fluorescence studies of Dy^{3+}-doped lead tellurborate glass, Journal of Luminescence 132 (2012) 86–90.