



Optical and luminescence properties of sodium lead alumino borosilicate glasses doped with Dy³⁺ ions

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Abstract - Glasses with the composition $20\text{Na}_2\text{O}-10\text{PbO}-(5-x)\text{Al}_2\text{O}_3-40\text{B}_2\text{O}_3-25\text{SiO}_2: x\text{Dy}_2\text{O}_3$ for $x = 0$ to 1.5 mol % were prepared in steps of 0.5 by the melt-quenching technique. The prepared glass samples were characterized by Photoluminescence, Optical absorption spectra. Optical absorption and luminescence spectra of all the glasses were recorded at room temperature. From the observed absorption edges optical band gap, the Urbach energies were calculated, the optical band gap is found to decrease with the concentration of Dy_2O_3 . The luminescence spectra exhibited conventional blue, yellow and red emission bands at around 482 nm, 575 nm and 662 nm corresponds to the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$, $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{11/2}$ transitions respectively. The effect of Dy^{3+} ion concentration on the intensity ratio of yellow to blue emission bands has also been studied. The emission spectra for different pumping wavelengths were characterized through Commission International d'Eclairage (CIE) 1931 chromaticity diagram to explore its suitability for WLED applications.

Keywords: Trivalent dysprosium (Dy^{3+}) ion, Glasses, Annealing, Judd-Ofelt parameters, Optical and Luminescence Properties

1. INTRODUCTION

Now a day, development of optical devices based on rare earth ions doped materials is one of the interesting field of research. Rare earth doped glasses are widely used as laser materials, sensors, solar concentrators, optical amplifiers, optical memory devices, magneto-optical devices, medical lasers, eye safe lasers, flat panel displays, fluorescent lamps, white LED's etc. [1-4]. Glasses doped with rare earth ions are proving to be luminescence materials as they have high emission efficiencies. These emissions correspond to 4f-4f and 4f-5d electronic transitions in the RE^{n+} . The 4f-4f transition gives an especially sharp fluorescence pattern from

the UV to the infrared region. This is due to shield effects of the outer 5s and 5p orbital's on the 4f electrons [5]. The Judd-Ofelt (JO) theory was shown to be useful to characterize radiative transitions for RE-doped solids and to estimate the intensities of the transitions for rare-earth ions. This theory defines a set of three intensity parameters, Ω_λ ($\lambda = 2, 4, 6$) that are sensitive to the local environment of the rare-earth ions. The rare earth doped materials is significant emphasis due to their potential applications in fields of laser technology, optoelectronic devices, fiber optic amplifiers, infrared to visible up-converters and phosphors [6]. Therefore luminescence properties of rare earth doped different glass hosts are being

prepared and investigated with the purpose to know their utility for luminescence applications. The visible luminescence of trivalent dysprosium (Dy^{3+}) mainly consists of narrow lines in the blue (470–500 nm, $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$) and yellow (570–600 nm, $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$) along with feeble red emission corresponding to (660 nm, $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{11/2}$) region [7]. The later one belongs to the Hyper sensitive transition ($L = 2, J = 2$), which is strongly influenced by the environment. Out of the 14 lanthanide elements, dysprosium in its trivalent state (Dy^{3+}) is an efficient emitter in the visible region and it is the only ion that emits two intense colors which on mixing in suitable proportions yields white light. At a suitable yellow-to-blue (Y/B) intensity ratio, Dy^{3+} ion can emit white light. Thus, luminescent materials doped with Dy^{3+} ion are usually used for generation of white light both in glasses and phosphors. By adjusting the Y/B intensity ratio, it is possible to obtain near white light emission in Dy^{3+} -activated luminescent nanophosphors [8]. The present work reports optical and luminescence properties of Dy^{3+} doped sodium lead alumino borosilicate glasses were characterized through optical absorption, excitation and emission spectral measurements. The radiative properties and symmetry around the RE-ions have been investigated using Judd-Ofelt (JO) theory and the radiative properties have been calculated. The characteristic of the emission color was examined through CIE 1931 chromaticity diagram. Decay curves of the $^4\text{F}_{9/2}$ energy level have been measured

and the possibility of energy transfer between Dy^{3+} - Dy^{3+} ions in the prepared glasses have also been discussed and reported.

2. MATERIALS AND METHODS

2. 1 Glasses preparation

The glass samples were prepared by the conventional melt quenching method with the following compositions. $20Na_2O\text{-}10PbO\text{-}(5-x)Al_2O_3\text{-}40B_2O_3\text{-}25SiO_2 - xDy_2O_3$ where $x= 0.5, 1.0$ and 1.5 mol\% . These glasses can be designated as NPABSDy0.5, NPABSDy1.0 and NPABSDy1.5 depending on the Dy^{3+} ion concentration from 0.5 to 1.5 mol% respectively. About 10 g of the batches of composition were taken and grounded thoroughly in an agate mortar to obtain homogenous mixture. The homogeneous mixture was then taken into a silica crucible and heated at 1200°C in an electrical furnace for 20 min until the homogeneous melt was obtained. This melt was then poured quickly on a brass mold and pressed quickly with another brass mold to obtain circular shaped glass samples with uniform thickness. The glass samples thus prepared were annealed at 400°C in order to make them free from thermal strains.

2. 2 Measurements

The optical absorption spectra were recorded on a JASCO UV-VIS-NIR spectrophotometer (model V-670) at room temperature in the range 200–1400 nm. The emission and excitation spectra for all the prepared glasses were recorded at room temperature using Shimadzu RF-5301 PC-Spectro fluorophotometer with a spectral resolution 0.5 nm. The time-resolved luminescence (PL) measurements were carried out using home-built setups with 385.6 nm laser as the excitation source. The emission from sample was coupled into a monochromator (Acton SP2300) coupled to CCD (charge coupled detector) through the appropriate lenses and filters.

3. RESULTS AND DISCUSSION

3.1 Optical absorption spectra and energy level analysis

The optical absorption spectra of Dy^{3+} doped NPABS glasses are shown in Fig. 1, respectively. The absorption spectra of the all glasses were found to be slightly difference in their intensity. From observation, the absorption intensity of the all bands increased with the increasing of Dy_2O_3 concentration. The spectra consists of in homogeneous absorption bands due to the transitions assigned from ground state, $^6H_{15/2}$ to various excited states of Dy^{3+} ions. In this present work, the absorption spectrum of Dy^{3+} ions shows totally nine absorption bands located at 384, 423, 446, 747, 796, 890, 1080, 1259 and 1656 nm due to

the $4f^9$ electronic transitions of the Dy^{3+} ions from the $^6H_{15/2}$ ground level to the various excited states such as $^4I_{13/2} + ^4F_{7/2}$, $^4G_{11/2}$, $^4I_{15/2}$, $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}$, ($^6H_{9/2} + ^6F_{11/2}$) and $^6H_{11/2}$ transitions, respectively [9]. As the concentration increases, the intensity of the absorption bands found to increase where as the band centre does not differ. The absorption transitions such as $^6H_{15/2} \rightarrow ^6F_{11/2}$ and $^6H_{15/2} \rightarrow ^6H_{11/2}$ are found to posses higher intensity which are highly sensitive to host environment known as hypersensitive transitions and obeys the selection rule $|\Delta S| = 0$, $|\Delta L| \leq 2$ and $|\Delta J| \leq 2$.

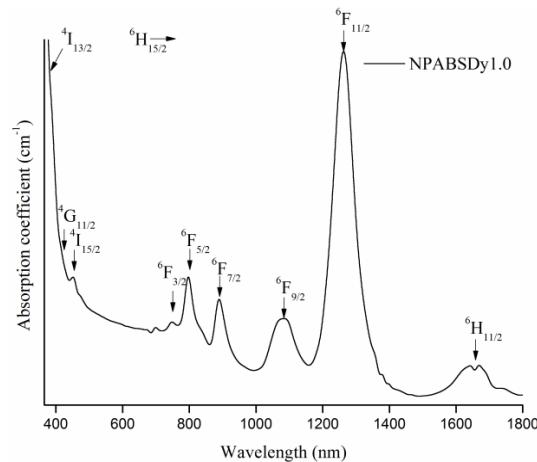


Fig. 1 Absorption spectra of the Dy^{3+} Doped NPABSDy1.0 glasses

3.2 Oscillator strengths and Judd-Ofelt analysis

The spectral intensity of the absorption bands are studied through the oscillator strengths (f_{exp}) values of the $f\text{-}f$ electronic transitions in the RE ions. The experimental oscillator strengths of the absorption bands are calculated from the relative areas under the absorption band of the individual transitions by using the expression,

$$f_{\text{exp}} = 4.318 \times 10^{-9} \int \varepsilon(v) dv \quad (1)$$

where $\varepsilon(v)$ is the molar absorptive of the band at a wave number v (cm^{-1}). The theoretical oscillator strength (f_{cal}) of the induced electronic dipole transition can be calculated from the Judd-Ofelt theory using the below given expression,

$$f_{\text{cal}} = \frac{[m^2 \cdot m]}{[m^2 \cdot m]} \left[\frac{[m^2 \cdot m]}{[m^2 \cdot m]} \right] \sum_{k=1}^6 \alpha_{k,1} \alpha_{k,2} \alpha_{k,3} \frac{[m^2 \cdot m]}{[m^2 \cdot m]} \frac{[m^2 \cdot m]}{[m^2 \cdot m]} \quad (2)$$

where m is the mass of the electron, c is the velocity of light in vacuum, v is the wave number (cm^{-1}) of the transition from the ground state (ψ_i) to the excited state (ψ_f), h is the plank's constant.



J is the total angular momentum of the ground state, n is the refractive index, $(n^2+2)^2/9$ is the lorentz local field correction account for the dipole-dipole transition, Ω_λ is the JO intensity parameter and $\|U^\lambda\|^2$ are the square reduced matrix elements of the unit tensor operator of the rank $\lambda = 2, 4$ and 6 which are estimated from the intermediate coupling approximation for the transition from (H_1) to (F_1) [10]. The intense transition lie between ${}^6\text{H}_{5/2}$ ground state and the ${}^6\text{H}$ and ${}^6\text{F}$ terms in the infrared region are spin allowed transitions ($\Delta S = 0$). The transition within the ${}^6\text{H}$ term are allowed by the selection rule on the orbital angular momentum ($\Delta L = 0$) and hence they are intense compared to other transitions. The experimental and calculated oscillator strengths ($\times 10^{-6}$) and the rms deviation (σ) of the title glasses have been calculated and presented in **Table 1**. It is observed that, the experimental and calculated oscillator strengths are having good agreement in the case of weak transitions. The spectral intensity of the ${}^6\text{H}_{11/2}$ hypersensitive transition is found to be more than the other transitions.

The J-O theory has been applied to the experimentally evaluated oscillator strengths to find the J-O intensity parameters (Ω_2 , Ω_4 and Ω_6) by least square fit analysis. The J-O intensity parameters and Spectroscopic quality factor ($\chi = \Omega_4/\Omega_6$) for the titled glasses are presented in **Table 2** along with the reported J-O parameters for other glasses [11]. The J-O intensity parameter are important to study the local structure and bonding nature of RE ions which indicates the covalence of metal ligand bond and also on the asymmetry of ion sites in the neighborhood of RE ion. The bulk properties such as viscosity and rigidity can be known through the magnitudes of Ω_4 and Ω_6 parameters measured using the J-O theory. From **Table 2**, it is observed that Ω_2 is higher than Ω_4 and Ω_6 and follows the trend $\Omega_2 > \Omega_6 > \Omega_4$ [12].

Table 1 Experimental and calculated oscillator strengths ($\times 10^{-6}$), Number of transition (N) and rms deviation (σ) of the Dy^{3+} -doped sodiumlead alumino borosilicate glasses.

S.No	Transition from ${}^6\text{H}_{15/2} \rightarrow$	λ nm	ν cm $^{-1}$	NPABSDy1.0 f_{exp}	NPABSDy1.0 f_{exp}
1	${}^6\text{H}_{11/2}$	1656	6038	1.3	1.483
2	${}^6\text{F}_{11/2} + {}^6\text{H}_{9/2}$	1259	7942	11.191	11.144
3	${}^6\text{F}_{9/2}$	1080	9259	1.601	1.582
4	${}^6\text{F}_{7/2}$	890	11235	1.457	1.751
5	${}^6\text{F}_{5/2}$	796	12562	0.922	0.933
6	${}^6\text{F}_{3/2}$	747	13386	0.161	0.188
7	${}^4\text{I}_{15/2}$	446	22421	0.06	0.10

8	${}^4\text{G}_{11/2}$	423	23640	0.10	0.07
9	${}^4\text{I}_{13/2} + {}^4\text{F}_{7/2}$	384	26041	0.12	0.09
10	δ_{rms}	± 0.01158			
11	N	9			

Table 2 Judd-Ofelt intensity parameters ($\Omega_\lambda \times 10^{-20}$ cm 2), spectroscopic quality factor (Ω_4/Ω_6) in NPABS glasses doped with dysprosium ions.

Sample code	J-O intensity parameters			Ω_4/Ω_6	Trend
	Ω_2	Ω_4	Ω_6		
NPABSDy [present]	14.49	1.26	2.23	0.5658	$\Omega_2 > \Omega_6 > \Omega_4$
0.5DPTFB [13]	10.21	1.73	2.12	0.8138	$\Omega_2 > \Omega_6 > \Omega_4$
DLCZFB [14]	11.25	2.45	5.16	0.4748	$\Omega_2 > \Omega_6 > \Omega_4$
LB [15]	10.43	2.19	3.53	0.6203	$\Omega_2 > \Omega_6 > \Omega_4$

3.3 Band gap and Urbach's energy analysis

The optical band gap is an important parameter in the field of photonics which gives information about the electronic structure of amorphous materials. The band gap energy values (E_{opt}) of the crystalline, amorphous materials can be evaluated from the fundamental absorption edges of the absorption spectral measurements through direct and indirect allowed transitions. Initially, the absorption edges shift towards the higher wavelengths side with the increase in Dy^{3+} ion content, ie the absorption edges exhibit red shift indicating the fact that the band gap values decreases. The Mott and Davis theory was used to derive a relation between the band gap and the absorption coefficient (α) and the same is expressed using the below given equation,

$$(\alpha h\nu)^n = B(E - E_g) \quad (3)$$

where α is the absorption coefficient, E is the energy of the applied photon, h is the plank's constant, ν is the frequency of the applied photon, B is the band tailing parameter, E_g is the band gap and n is equal to 2 or $1/2$ which signifies direct or indirect allowed transitions. The graph plotted between E and $(\alpha h\nu)^n$ are referred as Tauc's plot and Tauc's plot for the title glasses are shown in **Fig. 2** [16]. The linear portion of the Tauc's plot can be extrapolated to zero absorption and the intersection of E gives the optical band gap value. The calculated band gap values of the prepared glasses are presented in **Table 3**.

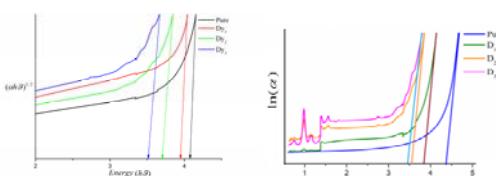


Fig. 2 Tauc's plot for the Dy^{3+} -doped NPABS glasses

3.4 Luminescence spectra

In order to analyze luminescence properties for the NPABSDy1.0 glasses, it is essential to know the suitable excitation wavelengths of Dy^{3+} ions. The luminescence behavior of Dy^{3+} -doped NPABS glasses have been studied throughout the emission spectral measurement. The luminescence spectra have been recorded by monitoring an excitation at 385 nm as a function of various Dy^{3+} ion concentrations and are shown in **Fig. 3**. The spectra contain three intense luminescence bands corresponding to ${}^4F_{9/2} \rightarrow {}^6H_J$ ($J = 15/2, 13/2$ and $11/2$) transitions located nearly the same wavelengths. In the blue region at 482 nm (${}^4F_{9/2} \rightarrow {}^6H_{15/2}$), yellow region at 575 nm (${}^4F_{9/2} \rightarrow {}^6H_{13/2}$) and a weak band in red region at 665 nm (${}^4F_{9/2} \rightarrow {}^6H_{11/2}$) are observed [17].

Table 3 The fundamental absorption edge (λ_{edge}), Optical band gap (E_{opt}) and Urbach's (ΔE) energy of the Dy^{3+} ions doped sodium lead alumino borosilicate glasses.

Sample code	λ_{edge} nm	Energy band gap (E_{opt}) (eV)		ΔE (eV)
		Direct	Indirect	
NPABS	316.5	3.9535	4.1833	0.2527
Dy0.5				
NPABS	320.5	3.8410	3.8212	0.2657
Dy1.0				
NPABS	323.0	3.8259	3.7621	0.2685
Dy1.5				

Table 4 Transition probability (A_R), luminescence branching ratio (β_R) and total transition probability (A_T) for the observed emission transitions for Dy^{3+} ions in sodium lead alumino borosilicate glasses

Transition	A_R (S^{-1})	β_R	A_T (S^{-1})
NPABSDy1.0			
${}^4F_{9/2} \rightarrow {}^6F_{15/2}$	161.8	0.1238	
${}^4F_{9/2} \rightarrow {}^6F_{13/2}$	955.03	0.7311	1306.27
${}^4F_{9/2} \rightarrow {}^6F_{11/2}$	124.98	0.0956	

3.5 White light stimulation

The luminescent intensity of the emission spectral measurements has been characterized using the CIE 1931 chromaticity diagram. **Fig. 4** shows the

CIE chromaticity diagram for the prepared glasses ($\lambda_{ext} = 393$ nm) and the values of the (x, y) color coordinates are found to be (0.34, 0.38), (0.34, 0.39) and (0.34, 0.39) corresponding to the prepared NPABSDy0.5, NPABSDy1.0 and NPABSDy1.5 glasses respectively. It is observed from figure that, the (x, y) color coordinate values are found to lie in the white light region.

The color temperature of a light source is the temperature of the planckian's black body radiator, whose radiation is the same chromaticity as the light source. The chromaticities of nature and artificial light sources, including day light are not on this locus, hence "correlated color temperature" (CCT) is used to indicate the temperature of the black body whose chromaticity is nearest to that of the light source. Generally white light deals with CCT from the planckian locus approximation, the range of CCT can be derived from CIE coordinates using the third power polynomial which is applied between 2222 K and 13,000 K and is given by the McCamy's approximate formula

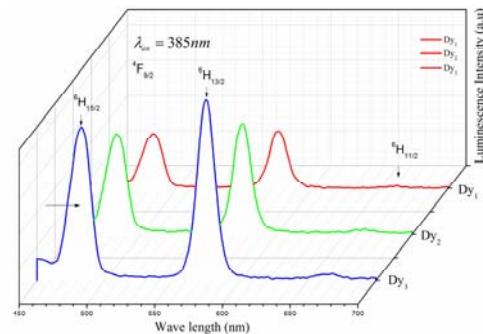


Fig. 3 Luminescence spectra of the Dy^{3+} doped NPABS glasses

$CCT(x, y) = -449n^3 + 3525 n^2 - 6823 n + 5520.33$
where $n = (x - x_e)/(y - y_e)$; ($x_e = 0.3320$ and $y_e = 0.1858$). The CCT values, color coordinates and Y/B values of the prepared glasses are calculated and presented in **Table 5**. The CCT values of the prepared glasses are found to be 5577, 5583 and 6420 K corresponding to the NPABSDy0.5, NPABSDy1.0 and NPABSDy1.5 respectively, under 393 nm excitation [18]. Further, CCT values for all the prepared glasses are found to be higher than 3935 K of fluorescent tube and exhibit values between 5500 K of the day light 6400 K of the commercially available WLEDs resulting the use of these glasses for warm white light applications [19, 20].

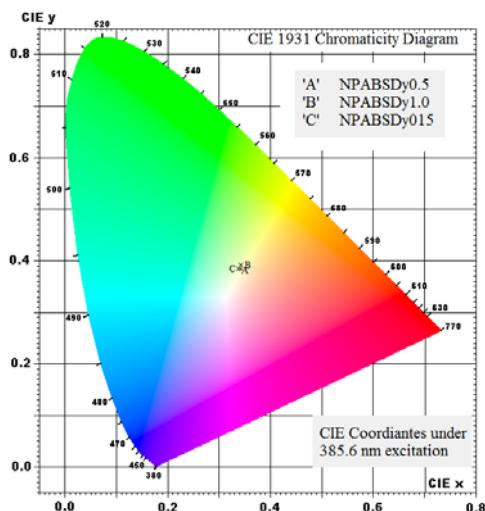


Fig. 5 CIE 1931 color chromaticity Diagram of the Dy³⁺-doped NPABS glasses.

Table 5 Glass label, yellow to blue intensity (Y/B) ratio, chromaticity coordinates (x, y) and correlated color temperature (CCT) for various Dy³⁺: systems

Glass label	Y/B ratio	Chromaticity		CCT (K)
		x	y	
NPABSDy1.0	1.11	0.34	0.39	5271 [present]
SLBiB10	0.97	0.44	0.42	3080 [21]
PKAZLFDy	0.77	0.32	0.37	5992 [22]

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CONCLUSIONS

The Dy³⁺ doped NPABS glasses were prepared at various doping concentration of Dy₂O₃ and characterized for their optical and luminescence properties. The absorption spectra consist of nine absorption bands corresponding to the transitions from the ground ⁶H_{15/2} ground level to the various excited states such as ⁴I_{13/2} + ⁴F_{7/2}, ⁴G_{11/2}, ⁴I_{15/2}, ⁶F_{3/2}, ⁶F_{5/2}, ⁶F_{7/2}, ⁶F_{9/2}, (⁶H_{9/2} + ⁶F_{11/2}) and ⁶H_{11/2} transitions, states of the Dy³⁺ ions. The emission band at 482, 575 and 665 nm were observed from

⁴F_{9/2} → ⁶H_{15/2} (blue), ⁴F_{9/2} → ⁶H_{13/2} (yellow) and ⁴F_{9/2} → ⁶H_{11/2} (red) transition respectively. The luminescence quenching were occurred with increasing of Dy₂O₃ concentration due to the increasing of non-radiative energy transfer thought cross-relaxation and resonant energy channel. The NPABS glass doped with 1.0 mol% of Dy₂O₃ gives the best result for luminescence properties. From Y/B ratio indicate that asymmetry nature in glass matrices. The Y/B ratio of all glass increased with increasing of Dy₂O₃ concentration, reflecting that the more symmetry nature in glasses also correlated color temperature (CCT) increases with increasing of Dy₂O₃ concentration. The (x,y) chromaticity coordinates of the prepared glasses lie in the white light region of the CIE1931color chromaticity diagram illustrating the generation of possible white light from the present Dy³⁺ doped glasses for white LED applications

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