Physical, Optical and Luminescence properties of Dy^{3+} doped Antimony Borate glass system

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Abstract

Binary glasses with the composition $40Sb_2O_3$-$60B_2O_3$: xDy_2O_3 for x = 0 and 0.5 mol% were prepared by the melt-quenching technique. The prepared glass samples were characterized by Photoluminescence and optical absorption spectra. Physical properties of the prepared glass samples were also done. From optical absorption spectra of the glass is recorded at room temperature shows six inhomogeneous absorption bands due to the absorption transitions of Dy^{3+} ions. These absorptions are assigned from ground state $^6H_{15/2}$ to various excited state of Dy^{3+} ions. From the figure we observed absorption peaks at 324, 349, 366, 388, 426 and 450nm. Among these 349 and 388nm are the strongest absorption peaks. These bands are attributed to $^6H_{15/2} \rightarrow {}^6P_{9/2}$, $^6H_{15/2} \rightarrow {}^6P_{7/2}$, $^6H_{15/2} \rightarrow {}^6P_{5/2}$, $^6H_{15/2} \rightarrow {}^4F_{7/2}$, $^6H_{15/2} \rightarrow {}^4G_{11/2}$, and $^6H_{15/2} \rightarrow {}^4I_{15/2}$ transitions respectively. From the observed absorption edges optical band gap, the Urbach energies were calculated. The luminescence spectra exhibited conventional blue, yellow and red emission bands at around 478 nm, 575 nm and 662 nm corresponds to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ transitions respectively. The effect of Dy^{3+} ion concentration on the intensity ratio of yellow to blue emission bands has also been studied. The luminescence spectra are studied under different excitation wavelengths. The emission spectra is characterized through Commission International d'Eclairage (CIE) 1931 chromaticity diagram to explore its suitability for display and WLED applications.

Keywords: *Trivalent ion, dysprosium, glasses, annealing, melt-quenching, optical, luminescence Properties*

1. Introduction

Glass is a network of atoms bonded to each other through covalent bonds with oxygen atoms. It is usually tetrahedral bonded together in a random arrangement. The glass transition from solid glass to the viscous liquid glass is an important property. Basically glass is an elastic solid below the transformation region and a viscous liquid above it. The structure of the solid has all the attributes of a liquid except that solid does not flow on any meaningful time scale. If glass is cooled from the melt faster, the overall glass structure will have a large volume (lower density) than one that is cooled slowly. Glass is an elastic solid without the

structural periodicity and long range order of crystalline material. It looks like a liquid but behaves like a solid.

Recent development of optical devices was based on rare earth ions doped materials is one of the interesting field of research. Rare earth doped glasses were used as optical device materials, sensors, solar concentrators, 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 rare earth^{n+}. The 4f-4f transition gives 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 lanthanum group doped materials is important because of their potential applications in the fields of optical device technology, optoelectronic devices, 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, $^4F_{9/2} \rightarrow {}^6H_{15/2}$) and yellow (570–600 nm, $^4F_{9/2} \rightarrow {}^6H_{13/2}$) 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 that on combining in appropriate proportions yields white light. At an appropriate yellow-to-blue (Y/B) intensity ratio, Dy^{3+} particle emits white light. Thus, light emitting materials doped with Dy^{3+} ion are used for generation of w-light 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 the optical and luminescence properties of antimony borate glass doped with Dy named here after as SbBDy0 and SbBDy0.5 glasses only, characterized through optical absorption, excitation and emission spectral measurements. The characteristics of the emission color were examined through CIE 1931 chromaticity diagram.

2. Materials and methods

2. 1 Glasses preparation

The glass samples were prepared by the standard melt quenching method with the following compositions. $(60\text{-}x)B_2O_3\text{-}40Sb_2O_3$: xDy_2O_3 where x= 0 and 0.5 mol%. The glass samples were named as SbBDy0 and SbBDy0.5 respectively. About 10 gm of the batches of composition were taken and grounded completely in an agate mortar to get homogenised mixture. The homogeneous mixture was then taken into a silica crucible and heated at 1000^{o}C in an electrical furnace for 10 min until the homogeneous melt was obtained. This soften was then poured quickly on a brass mildew and ironed quickly with another brass mildew to get circular formed glass samples with uniform thickness. The glass samples thus prepared were annealed at 400^{o}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 within the range 200–2000 nm with a scanning speed 100nm/min. The emission and excitation spectra for all the prepared glasses were recorded at room temperature using Shimadzu RF-5301 PC-Spectrofluorophotometer with a spectral resolution 0.5 nm. The CIE colour co-ordinates were drawn using Radiant Imaging software version 2.0.

3. Results and discussion

3.1. Physical Properties

Density of glass is generally explained in terms of competition between the masses and the volumes of the various structural groups present in it. Therefore, density is related to how tightly the atoms and atomic groups are placed together in the glass network. For the glasses considered in this article, the density (ρ) increases systematically by substituting B_2O_3 with Dy_2O_3, as reported in Table 1.

Table 1 Physical Properties of the synthesized samples

S.No	Parameter	Sample code	
		SbBDy0	SbBDy0.5
1	Density (ρ) g/cm^3	3.5314	3.7303
2	Molar volume (V_m) cm^3/vol	1.5697	1.5668
3	Dopant ion concentration (N_i)x10^{20}	---	0.7025
4	Inter ion separation (R_i) x10^{-7}	---	2.4234
5	Polaron radius (R_p) x10^{-7}	---	0.9764
6	Field strength (F_i)x10^{14}	---	3.1462
7	Reflection Loss (R)	0.03697	0.04537
8	Dielectric constant (ε)	3.02000	3.2833
9	Molar refractivity (R_m)	16.4879	18.5248
10	Electronic polarizability x10^{-22}	--	0.14693
11	Average Molecular weight	158.379	159.895
12	Refractive Index (n_d)	1.747	1.755

3.2 Optical absorption spectra and energy level analysis

The optical absorption spectra of SbBDy0 and SbBDy0.5 glasses are shown in Fig. 1A and 1B respectively.

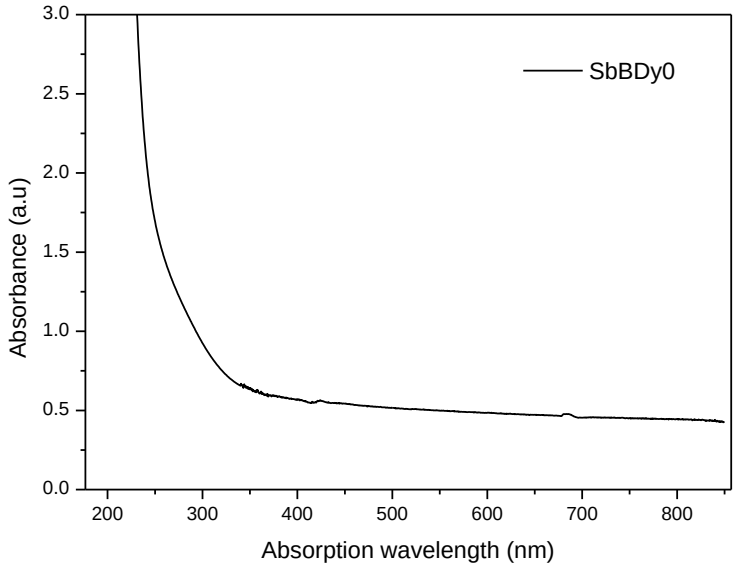

Fig. 1A Optical absorption spectrum of SbBDy0 glass

From Fig. 1A the spectra consist of SbBDy0 sample does not show any absorption bands. Figure 1B show the optical absorption spectrum of SbBDy0.5 glass sample in the range from 250 – 550nm at room temperature. We studied optical absorption studies in visible region only. The optical absorption edges are not sharply defined in glass sample, in accordance with their amorphous nature. The spectrum consists of six inhomogeneous absorption bands due to the absorption transitions of Dy^{3+} ions. These absorptions are assigned from ground state $^6H_{15/2}$ to various excited state of Dy^{3+} ions. From the figure we observed absorption peaks at 324, 349, 366, 388, 426 and 450nm. Among these 349 and 388nm are the strongest absorption peaks. These bands are attributed to $^6H_{15/2} \rightarrow {}^6P_{9/2}$, $^6H_{15/2} \rightarrow {}^6P_{7/2}$, $^6H_{15/2} \rightarrow {}^6P_{5/2}$, $^6H_{15/2} \rightarrow {}^4F_{7/2}$, $^6H_{15/2} \rightarrow {}^4G_{11/2}$, and $^6H_{15/2} \rightarrow {}^4I_{15/2}$ transitions respectively.

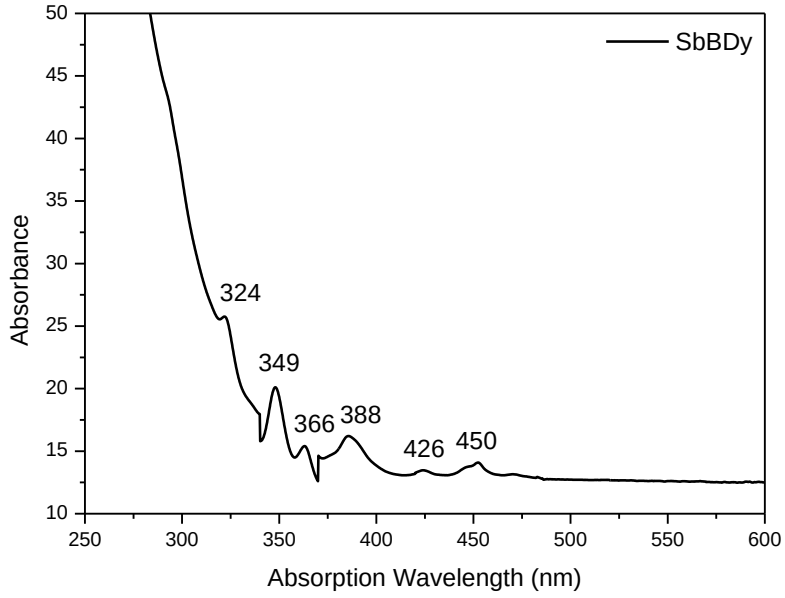

Fig. 1B Optical absorption spectrum of SbBDy0.5 glass

3.3 Band gap and Urbach's energy analysis

The optical band gap is a vital parameter within the field of photonics which provides data regarding the electronic structure of amorphous materials. The band gap energy values (E_{opt}) of the crystalline, amorphous materials are often evaluated with the help of the fundamental absorption edges through direct and indirect allowed transitions. Initially, the absorption edges shift towards the upper wavelengths side with the rise in Dy^{3+} particle 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 coefficient of absorption (α) and also the same is expressed using the equation, $(\alpha h\upsilon)^n = B(E-E_g)$ where α is the absorption coefficient, E is the energy of the applied photon, h is the plank's constant, υ 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. Fig. 2A and Fig. 2B are the graphs plotted between E and $(\alpha h\upsilon)^n$ referred as Tauc's plot and Tauc's plot for the title glasses [10]. The linear portions of the Tauc's plot are often workout to zero absorption and also the intersection of E provides the optical band gap value. The calculated band gap value of the prepared glass is presented in Table 2**.**

Table 2 The fundamental absorption edge (λ_{edge}), Optical band gap (E_{opt}) and Urbach's (ΔE) energy of the Dy^{3+} ions doped antimony borate glass

S.No	Absorption Edge (nm)	Optical Bandgap E (eV)		Urbach Energy ΔE (eV)
		Direct	Indirect	
1	399	2.84	2.78	0.06

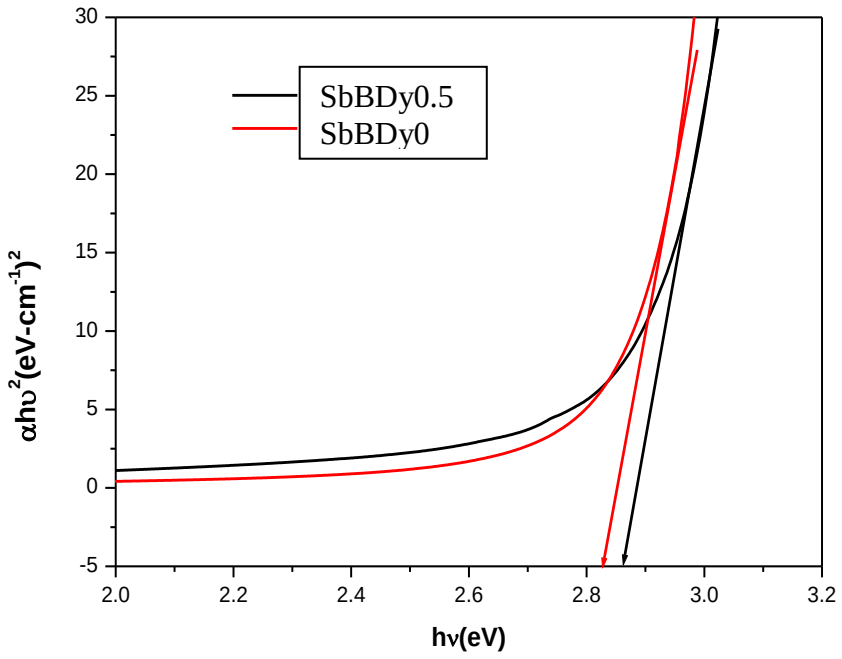

Fig. 2A

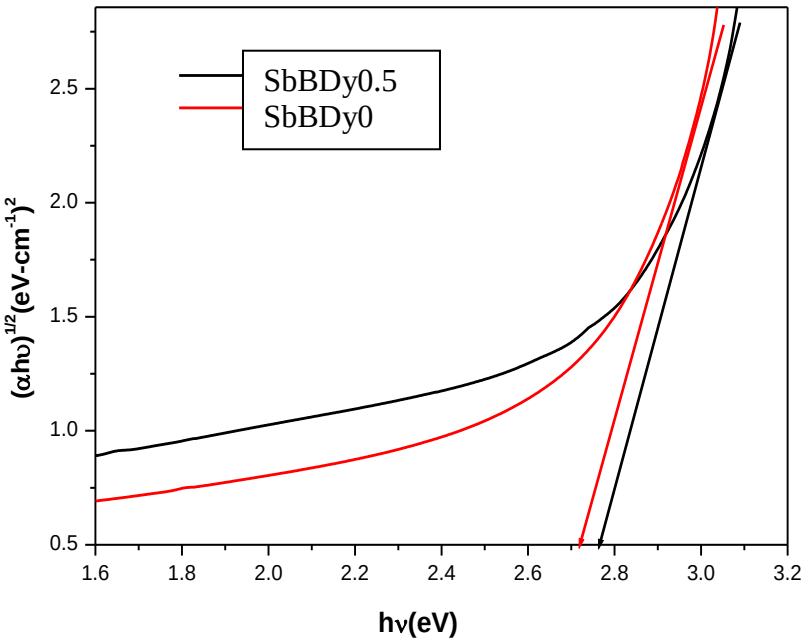

Fig. 2B

Where A may be a constant and E_g is outlined because the energy band gap. A typical plot of $(\alpha h\upsilon)^2$ versus hυ for the glass having 60% B_2O_3 is presented in Figure 3A. Extrapolation of this plot to $a^2 = 0$ provides the optical band gap E_g for direct transition. We have estimated the optical band gap for all the glasses, which varies from 2.8 - 3.0 eV for direct transition. The value of E_g for indirect transition is obtained by extrapolation of $(\alpha h\upsilon)^{1/2}$ versus hυ plot to $a^{1/2} = 0$ as shown in the Figure 3B. The optical band for indirect transition varies from 2.7 - 2.8 eV. This can be attributed to the structural changes that are taking place with the introduction of rare earth ions. Inclusion of rare earth ions in borate structure may create some defect states in the midgap, which is responsible for the decrease of bandgap. The broadness of the absorption edge may be due to the presence of localized state in the band tails.

Here 'E' is the Urbach energy which indicates the width of the band tails of the localized states and depends on temperature, induced disorder, static disorder and on average photon energies. Hence, Urbach energy provides a measure for the disorder in amorphous and crystalline materials [11]. The nature of disorder is different for crystalline and amorphous solids. In amorphous solids, the static atomic structural disorder dominates and can be due to presence of defects like dangling bonds or non-bridging oxygens in glasses [12]. Urbach energies (ΔE) are calculated by taking the reciprocals of the slopes of linear portion in the lower photon energy regions of the curves as shown in Figures 4A & 4B. It shows the structural disorder of the system. Smaller is the value of Urbach energy, greater is the structural stability of the glass system. It is observed that the SbBDy0.5 glass has low value of structural disorder, which indicates the strong structural stability.

3.4 Photoluminescence studies

3.4.1 PLE and PL studies of SbBDy0.5 glass

575nm wavelength monitored PL excitation spectrum of the SbBDy0.5 glass is measured using a Xenon as excitation source at room temperature is as shown in **Figure 3**. From the figure several bands were observed in the visible region at 324, 349, 366, 388, 411, 426nm. Among these 388nm peak is strongest one and the transitions were assigned to $^6P_{3/2}$, $^6P_{5/2}$, $^6P_{7/2}$, $^4F_{7/2}$, $^4G_{9/2}$ and $^4G_{11/2}$ respectively.

Figure 4 is the emission spectrum of SbBDy0.5 glass measured at 280nm excitation wavelength. From the figure two emission bands were observed in the visible region one is broad band range from 375 – 500nm peaking at 468nm which belongs to blue and the second one is a sharp band at 562nm belongs to yellow. These two emission bands are the characteristic emissions of Dy^{3+} ion and were assigned to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ respectively. Finally the glass emits cyan colour which is very close to the white light.

Figure 5 is the emission spectrum of SbBDy0.5 glass measured at 388nm excitation wavelength. From the figure two emission bands along with two humps were observed in the visible region one is broad band peaking at 478nm which belongs to blue and the second one is a sharp band at 575nm belongs to yellow and two small bands at 548nm (green) and 662nm (red). These emission bands are the characteristic emissions of Dy^{3+} ion and were assigned to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (blue), $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (yellow) and $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (red) respectively. The emission intensities of blue and yellow were almost equal, where as the red emission intensity is negligible when compared to blue and yellow. But from the emission spectrum under 388nm excitation one green band is observed at 548nm which is interesting and a noval finding which is an interesting one. Finally the glass emits white colour which we can see in the CIE diagram shown in the section 3.5.

Figure 6 is the PL emission spectrum of the SbBDy0.5 glass measured at 460nm as excitation source at room temperature. The PL emission spectrum was measured range from 550nm to 900nm wavelength to know the emissions were useful for LED applications. It exhibit emission peaks at 575nm, 627nm in the visible region and emissions at 755, 848 and 882nm in the IR region.

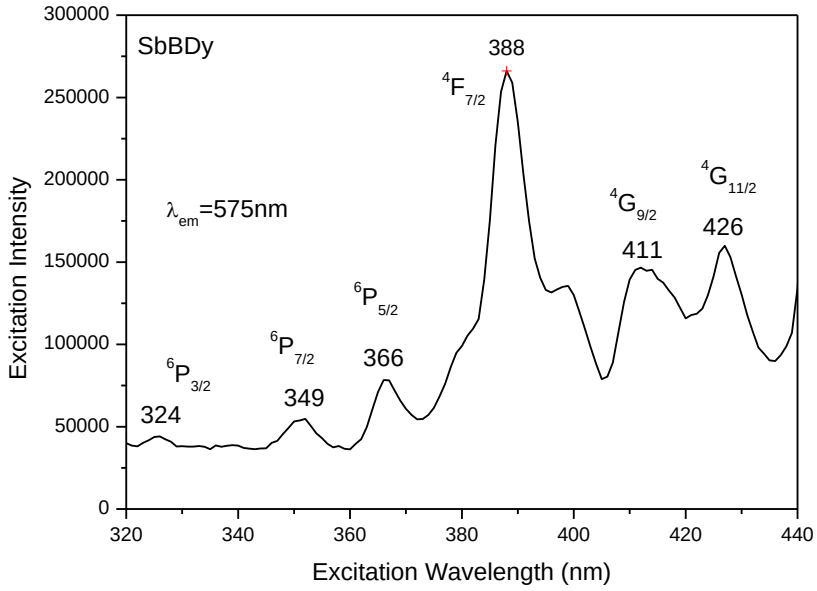

Figure 3 Excitation spectrum of SbBDy0.5 glass monitored at 575nm wavelength

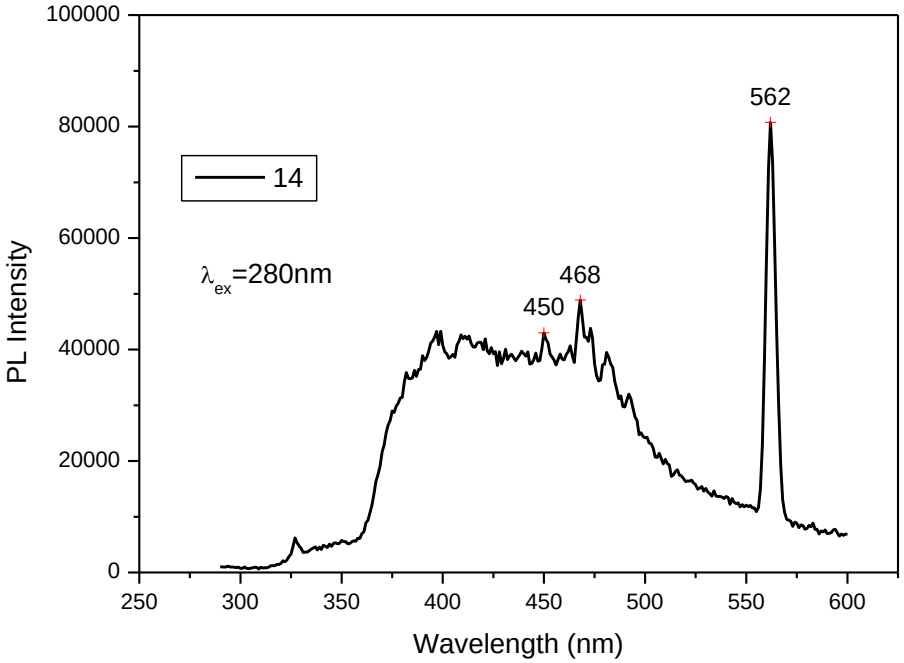

Figure 4 Emission spectrum of SbBDy0.5 glass at 280nm excitation wavelength

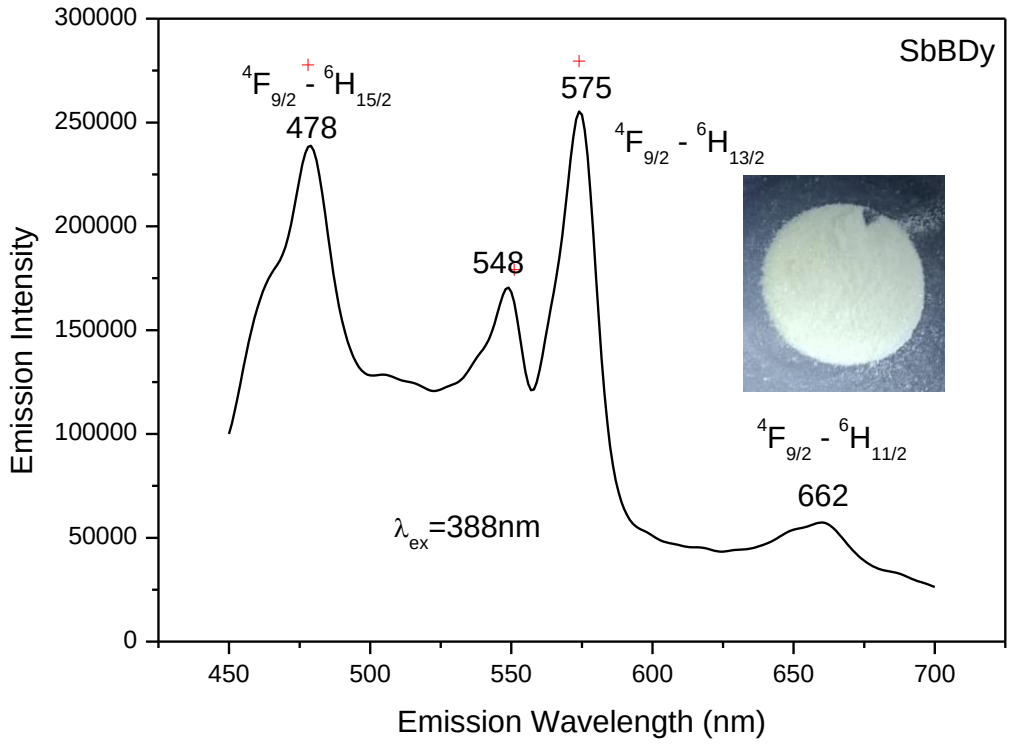

Figure 5 Emission spectrum of SbBDy0.5 glass at 388nm excitation wavelength

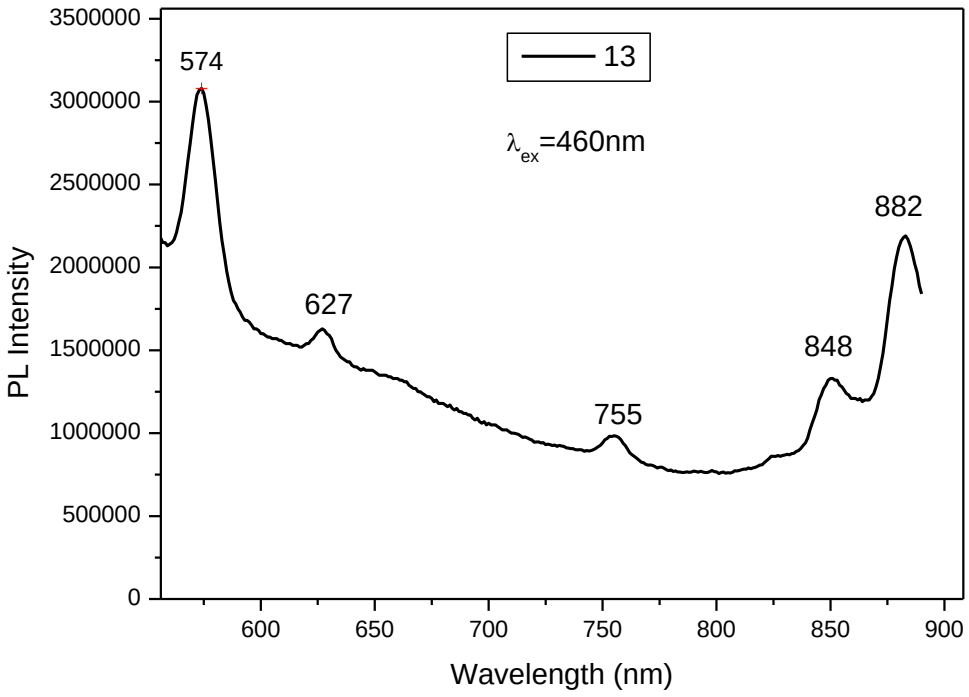

Figure 6 Emission spectrum of SbBDy0.5 glass at 460nm excitation wavelength

3.5 CIE analysis

3.5.1 CIE analysis of SbBDy0.5 glass

The CIE chromaticity coordinates is measured using emission spectra under the excitation of 388 nm. **Figure 7** represents the CIE chromaticity with colour coordinates of the glass sample. The prepared glass sample, SbBDy0.5 shows highest intensity having chromaticity co-ordinates X=0.285 and Y=0.325 close to the white spot in the chromaticity diagram. From the CIE plot, it is observed that prepared glass sample emit white light under the excitation of 388 nm. Such glass can be applicable for the white LED. Generally the ratio of ED transition to the MD transition is a measure of symmetry orientation of the local environment around the RE ion site. The calculated Yellow/Blue (Y/B) intensity ratio ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) / ($^4F_{9/2}\rightarrow{}^6H_{15/2}$) value is 1. Y/B ratio depicts the local environment site symmetry and the electro-negativity of the surrounding ligands.

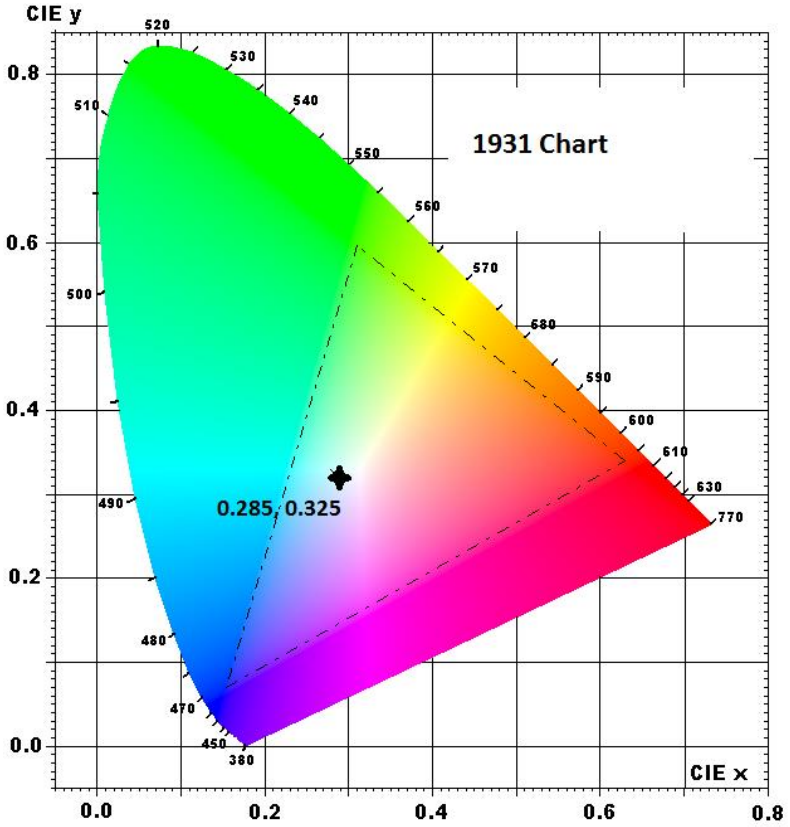

Figure 7 CIE Co-ordinates of SbBDy0.5 glass depicted on 1931 chart

The Correlated Colour Temperature (CCT) is calculated of the glass using CIE chromaticity coordinates (x and y) by McCamy's relation as below [38, 39]. CCT = -437 n^3+ 3601 n^2- 6861 n + 5514.3 where, n= (x - 0.3320)/(y - 0.1858) and x, y are the CIE chromaticity co-ordinates. The CCT of glass SbBDy0.5 is 8421 K, which is close to the CCT of standard white light illuminants. It is concluded that this glass can be useful for the preparation of white LED with highest emission intensity and more brightness.

Conclusions

The following conclusions were obtained

1. The SbBDy0.5 and pure SbBDy0 glasses were prepared and characterized for their optical and luminescence properties using melt quenching technique successfully.
2. From the value of Urbach energy, it is observed that the SbBDy0.5 glass has low value of structural disorder, which indicates the strong structural stability.
3. From the observed absorption peaks at 324, 349, 366, 388, 426 and 450nm, among these 349 and 388nm are the strongest absorption peaks. These bands are attributed to $^6H_{15/2} \rightarrow {}^6P_{9/2}$, $^6H_{15/2} \rightarrow {}^6P_{7/2}$, $^6H_{15/2} \rightarrow {}^6P_{5/2}$, $^6H_{15/2} \rightarrow {}^4F_{7/2}$, $^6H_{15/2} \rightarrow {}^4G_{11/2}$, and $^6H_{15/2} \rightarrow {}^4I_{15/2}$ transitions respectively.
4. From the figure several bands were observed in the visible region at 324, 349, 366, 388, 411, 426nm. Among these 388nm peak is strongest one and the transitions were assigned to $^6P_{3/2}$, $^6P_{5/2}$, $^6P_{7/2}$, $^4F_{7/2}$, $^4G_{9/2}$ and $^4G_{11/2}$ respectively.
5. The emission band at 478 and 562nm were observed from $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions respectively. From the emission spectrum under 280nm excitation wavelength, the cyan band is sharp with double intensity than the blue band intensity.
6. The SbBDy0.5 glass gives the good result for luminescence properties.
7. The (x,y) chromaticity coordinates of the prepared glass consist in the cyan light region of the CIE1931color chromaticity diagram indicating the glass is useful in display and w-LED applications under different excitations.

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