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White light-emitting Dy³⁺-doped transparent chloroborosilicate glass: synthesis and optical properties

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Abstract

Dy³⁺-doped chloroborosilicate glasses with the composition 35.7SiO₂-25.5B₂O₃-17BaO-3.4K₂O-3.4Al₂O₃-15BaCl₂ (mol%) were prepared using melt quenching technique. The glass transition temperature (T_g) was ~610°C. In UV-Vis-NIR absorption spectra characteristic absorption bands of Dy³⁺ appeared at 322, 347, 364, 388, 795 and 880 nm due to spectral transitions from the ⁶H_{15/2} level to various higher levels of Dy³⁺ ion. The excitation spectrum was recorded at within 200–550 nm by monitoring emissions at 576 nm. The excitation bands at 392, 428, 453 and 472 nm were attributed to the ⁶H_{15/2} → ⁴I_{13/2}, ⁴G_{11/2}, ⁴I_{15/2} and ⁴F_{9/2} transitions, respectively. Prominent emission bands were observed at wavelengths of 484, 576, 664 and 754 nm when excited at 447 nm. The bands correspond to the transitions ⁴F_{9/2} → ⁶H_{15/2}, ⁴F_{9/2} → ⁶H_{13/2}, ⁴F_{9/2} → ⁶H_{11/2}, and ⁴F_{9/2} → ⁶H_{9/2}, ⁶F_{11/2} respectively. The emitted light from all the samples were found to be white. Their colour coordinates lie within the white range. The sample containing 0.5 wt% Dy₂O₃ emitted white light with the colour coordinates x=0.351, y=0.335, which are the very closest to pure white light and whose colour temperature of 4716 K is similar to daylight. Such white light-emitting transparent glasses promise to be enormously useful for various photonic applications.

Keywords: Dy³⁺-doped glass, chloroborosilicate glass, white light generation, absorption spectra, photoluminescence

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1. Introduction

Rare earth-doped glasses are excellent luminescent materials because of the occurrence of sharp fluorescence in the ultraviolet (UV), visible and infrared (IR) regions due to the shielding effects of their outer 5s and 5p orbitals on 4f electrons. These glasses have potential applications due to their emission efficiencies of 4f→4f and 4f→5d electronic transitions in the RE ion. The Dy³⁺ ion is one of the most studied rare earth ions. Special attention has been focused recently on the study of Dy³⁺-doped glass scintillators for radiation measurement and homeland security applications as well as for dose monitoring for X-rays and protons [1]. Dy³⁺-activated glasses and glass phosphores [2,3] have also been studied for obtaining white light as well as for blue and yellow laser emissions which find applications in the fields of biomedicine and astronomy. Dy³⁺-ions can be excited easily due to the presence of abundant 4f→4f electronic bands [4]. The emission spectrum of Dy³⁺ ions consists mainly of strong bands corresponding to the ⁴F_{9/2}→⁶H_{15/2} (blue) and ⁴F_{9/2}→⁶H_{13/2} (yellow) transitions accompanied by a weak ⁴F_{9/2}→⁶H_{11/2} (red) transition in the visible range. Numerous Dy³⁺-doped glass systems therefore were studied for obtaining white light through appropriate combinations of these luminescent band intensities [5] and two primary-colored luminescent materials. The spectroscopic properties of rare earth ions depend on their 4f-4f transitions and can be controlled by changing the chemical composition of the host glass matrix.

The luminescence properties of Dy-doped high silicate glass were investigated by Nagli et al. who observed visible luminescence around 570 nm with 447 nm excitation [6]. The optical properties resulting from Dy³⁺ doping in the PbO-PbF₂ oxyfluoride glass matrix were investigated by Nachimuthu et al. the first of the two most dominant emissions of Dy³⁺ is the blue emission at 481 nm due to the ⁴F_{9/2} → ⁶H_{15/2} transition and the second appears in the yellow range at 575 nm due to the ⁴F_{9/2} → ⁶H_{13/2} transition [7]. Spectroscopic properties of Dy³⁺ ions in

lithium borate and lithium fluoroborate glasses were presented by Babu et al. [8]. The fluorescence properties of Dy^{3+} ions in two concentrations (1.0 and 0.1 mol%) have been investigated in a variety of borate and fluoroborate glasses modified with lithium, zinc, and/or lead. The fluorescence spectra emitted by the Dy^{3+} ions embedded in title glasses, when excited with a 457.9 nm laser, consist of ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_J$ transitions in the visible and near infrared ranges of the spectrum. The blue (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$) at ~ 485 nm and yellow (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$) at ~ 575 nm emission transitions are relatively more intense than the other emission transitions (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2,9/2,7/2}$) observed in the red and near infrared regions [9]. The photoluminescence properties of Dy^{3+} -doped transparent oxyfluoride alumino-silicate glasses have been reported by Lakshminarayana et al. A bright fluorescent yellow emission at 575 nm (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$) and a blue emission at 484 nm (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$) have been observed [10]. It was also observed, that strong blue 484 nm and yellow 574 nm emission bands appear in the Dy^{3+} doped $\text{ZnO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ (ZBP) glasses upon various excitations. Combination of these blue and yellow bands produces white light to the naked eye. It was found that $\text{ZnO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses emit white light efficiently under 400 and 454 nm excitations, which are closely matched with the emissions of commercial GaN blue LEDs and InGaN LEDs, respectively [11]. Optical properties of Dy^{3+} -doped phosphate and fluorophosphates glasses have been investigated. A strong yellow emission was observed from the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transition of Dy^{3+} ions in these glasses [12]. Dy-doped oxyfluoride glasses and nanocrystalline glass ceramics were found to emit intense white light when the ${}^4\text{F}_{9/2}$ level is inundated with 451 nm laser light. The chromaticity color coordinates of the visible emissions were calculated and found to be in the white light zone [13]. It was observed from the emission spectra of calcium fluoroborate (CFB) glasses doped with different concentrations of Dy^{3+} ions that the samples emit intense yellowish light which is close to white light [14]. The spectroscopic properties of silicate glasses doped with different concentrations of Dy^{3+} ions were studied. Simulation of white light for these glasses was also performed by varying the excitation wavelength. The results showed that the white light luminescence could be tuned to various wavelength excitations, making the glass suitable for generation of white light for blue LED chips [15]. Lead tungsten tellurite (LTT) glasses doped with different Dy^{3+} ion concentrations also show the usual characteristic absorption and emission bands of Dy^{3+} and emit white light [16]. The optical properties of Dy^{3+} -doped lead phosphate glasses were also reported. The yellow-to-blue emission intensity ratios and CIE chromaticity coordinates were

calculated and used to evaluate white light emissions as a function of the activator (Dy^{3+}) ion concentration [17]. Niobium phosphate glasses doped with different concentrations of Dy^{3+} ions have been synthesized and characterized to evaluate their fluorescence properties and determine their suitability for white light-emitting diodes (LEDs) [18]. White light emissions by dysprosium-doped lanthanum calcium phosphate oxide and oxyfluoride glasses were reported by Luewarasirikul et al. The emission spectra, excited with a 349 nm excitation wavelength, showed two major peaks corresponding to 482 nm blue and 574 nm yellow emissions. The (x,y) color coordinates under the 349 nm excitation wavelength were (0.38, 0.43) for both glass samples, which is in the white range of the CIE 1931 chromaticity diagram. The CCT values obtained from the glass samples were 4204 K for oxide glass and 4228 K for oxyfluoride glass which corresponds to commercial cool white light (3100 -4500 K) [19]. The spectroscopic properties of Dy^{3+} -doped $\text{Li}_2\text{O-B}_2\text{O}_3$ glasses were studied for white light-emitting material applications. The colour coordinates (x, y) of the studied glass samples were found to be (0.37, 0.40), which fall in the white light range of the chromaticity diagram [20]. Dy^{3+} -doped lithium borate glasses were studied for white LED applications. The CIE chromaticity chart shows that glass containing 0.5 mol% Dy_2O_3 has the colour co-ordinates $x = 0.33$ and $y = 0.37$, which are nearly equal to those of pure white light. All these glasses produce emission in the white range and can thus be used for bright white LED's and modern white LED bulbs [21].

From the above discussion it can be inferred that Dy^{3+} -doped glasses offer immense promise for photonic applications, especially as white light-generating materials. It will therefore be worthwhile to dope some new glass systems with Dy^{3+} and study their absorption and emission properties to find new white light-emitting materials. In response to this motivation, we investigated the synthesis and characterization of Dy^{3+} ion-ingrained low-phonon chloroborosilicate glass matrix with the composition $35.7\text{SiO}_2\text{-}25.5\text{B}_2\text{O}_3\text{-}17\text{BaO}\text{-}3.4\text{K}_2\text{O}\text{-}3.4\text{Al}_2\text{O}_3\text{-}15\text{BaCl}_2$ (mol%). We chose this composition because it is a new, stable and transparent glass, which is also known to have low phonon energy, as reported earlier [22]. Different concentrations of Dy^{3+} have been incorporated in the glass. We characterized the transparent Dy^{3+} -doped glasses by density measurement, x-ray diffraction, differential scanning calorimetry, dilatometry, refractive index measurement, UV-Vis-NIR absorption spectra, excitation spectra and emission spectra. Visible luminescence of a white colour was observed in all the samples at

447 nm excitation. These glasses are potential materials for various photonic applications, including white light emitters, i.e., WLED (white light-emitting diodes).

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2. Experimental

2.1 Glass preparation

Chloroborosilicate glass (CBS) with the composition $35.7\text{SiO}_2\text{-}25.5\text{B}_2\text{O}_3\text{-}17\text{BaO-}3.4\text{K}_2\text{O-}3.4\text{Al}_2\text{O}_3\text{-}15\text{BaCl}_2$ (mol%) was prepared using the melt quenching technique from quartz, SiO_2 (GR, Bremthaler, Quarzitwerk, Usinger, Germany), boric acid, H_3BO_3 (GR, 99%, Loba Chemie, Mumbai, India), barium carbonate, BaCO_3 (GR, 99%, Fluka Chemie GmbH, Buchs, Switzerland), potassium carbonate, K_2CO_3 (GR, 99%, Loba Chemie, Mumbai, India), aluminium oxide, Al_2O_3 (GR, Aldrich Chemical Company Inc, Milwaukee 53233, USA) and barium chloride, $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$ (GR, Dihydrated extra pure, Loba Chemie, Mumbai, India) as the raw materials. They were used directly with no further purification. 60 g of glass was prepared by melting well-mixed batches of the calculated composition in a high-purity alumina crucible at 1250°C for 1.5 h with intermittent stirring for 0.5 min in air in a raising hearth electric furnace. The molten samples were cast into an iron plate in air and annealed at 550°C for 2 h in order to remove the residual thermal stresses, followed by a slow cooling down to room temperature. Five more glasses of the same composition were prepared with the addition of (i) 0.1, 0.3, 0.5, 0.7 and 1 wt% Dy_2O_3 in excess (GR, 99%, Loba Chemie, Mumbai, India) using the same procedure and annealed at 550°C following the same schedule. The monolithic glasses thus obtained were cut and polished into the shapes and sizes required for the different characterizations, as described below.

2.2 Characterization

Differential scanning calorimetric experimentation was performed with a differential scanning calorimeter (NETZSCH Model STA 449 Jupiter F3, NETZSCH-Gerätebau GmbH, Selb, Germany) using powdered sample within the temperature range of $30^\circ\text{-}900^\circ\text{C}$ in a nitrogen atmosphere at a heating rate of 10 K/min. The coefficient of thermal expansion (CTE, α), glass transition temperature (T_g), and dilatometric deformation temperature (T_d) were measured using a horizontal vitreous silica dilatometer (DIL 402C, Netzsch-Gerätebau GmbH, Bavaria, Germany) at a heating rate of 4 K/min by heating a cylindrical sample approximately 25 mm length and 5 mm diameter at a rate of 4 K/min up to the temperature at which the glass softened,

after calibration with standard alumina supplied with the instrument by the manufacturer. The T_g and T_d values were reproducible within ± 1 °C for all samples. The X-ray diffraction (XRD) patterns of the bulk samples were recorded in an X'pert Pro MPD diffractometer (PANalytical, Almelo, the Netherlands), operating at 40 kV and 30 mA, using Ni-filtered CuK α radiation with the X'celerator, with a step size of 0.05°(2 θ) and a step time of 0.5s, at 10° to 80°. The UV-Vis absorption spectra and the PL spectra of all the samples were studied using polished 2 mm thick samples with the use of a fiber optic spectrometer (AvaSpec-3648-USB2, Avantes) and diode lasers with a 447 nm wavelength source. Photoluminescence spectrophotometer (model: custom made Quantum-Master: Enhanced NIR of Photon Technologies International, Canada) was employed for recording of the excitation spectra.

3. Results and Discussion

The compositions and physical properties of the glasses with the general composition 36.75SiO₂-26.25B₂O₃-20BaO-3.5K₂O-3.5Al₂O₃-12.5BaCl₂ (mol%) are listed in Table 1. All the samples were obtained as colourless, transparent monoliths. Figure 1 shows photographs of the prepared samples.

Table 1. Composition and physical properties of samples

Sample ID	Dy ₂ O ₃ Content (wt%)	Colour	Form
CBS	-	Colourless	Transparent monolith
CBSD1	0.1	Colourless	Transparent monolith
CBSD2	0.3	Colourless	Transparent monolith
CBSD3	0.5	Colourless	Transparent monolith
CBSD4	0.7	Colourless	Transparent monolith
CBSD5	1.0	Colourless	Transparent monolith

3.1 Density

The densities (ρ) of the glass samples were determined by the standard Archimedes principle. The measurements were done using a single pan balance and distilled water as an immersion liquid. The densities were obtained from the following relationship:

$$\rho = a \rho_x / (a-b) \quad (1)$$

where a is the weight of the glass sample in air, b is the weight of the glass sample when suspended in distilled water (density of water, $\rho_x = 0.997604 \text{ g}\cdot\text{cm}^{-3}$ at 25°C). Their densities are in the range of $3.5\text{-}3.6 \text{ g}\cdot\text{cm}^{-3}$. The density of the glasses did not vary much as their composition was almost the same. The base glass composition was the same for all samples, only only very small variations in rare earth content that do not have visible impact on the density of the glass. A very slight variation was observed in the 4th decimal place. The measured densities are listed in Table 2.

3.2 Differential Scanning Calorimetry and Dilatometry

Differential scanning calorimetry (DSC) was performed to determine the T_g and thermal behaviour of the glass by heating finely ground powder of the base glass (CBS) at the rate of $10\text{K}/\text{min}$ from $30\text{-}900^\circ\text{C}$. The DSC thermogram is shown in Fig 2(a). T_g was determined to be about 612°C .

The glass transition temperature (T_g) and dilatometric softening point (T_d) of CBS were measured by dilatometric measurement by heating a cylindrical sample approximately 25 mm in length and 5 mm in diameter at a rate of $4\text{K}/\text{min}$ up to the temperature at which the glass softened. Figure 2(b) shows the dilatometric curve of the glass. T_g and T_d were determined to be around 610° and 650°C , respectively. The T_g determined by dilatometry and DSC are closely similar temperatures.

3.3 XRD

The formation of the glasses was explicitly determined by XRD analysis. Figure 3 shows the XRD patterns of all the samples. The hump between $2\theta = 20^\circ\text{-}35^\circ$ indicates amorphosity of

the glasses. The presence of this hump and absence of any peaks in the samples indicate that they are amorphous in character and can be considered to be glasses.

3.4 Refractive Index

The Refractive index (n_i) at different wavelengths was measured for all the transparent glasses by Prism coupler using lasers of five different wavelengths. Figure 4 shows the variations in the refractive indices of different glasses with respect to wavelength. The refractive indices are in the range of 1.6064-1.6195 for a 532 nm wavelength. The n_i shows a very slight gradual increase with increases in the Dy_2O_3 content. It is evident that the value of n_i shows no noticeable change as there are only very slight variations in the compositions of the samples and their densities are almost identical. The n_i of any particular medium is the ratio of the velocity of light through the vacuum (c) to the velocity of light through the medium (v).

$$n_i = c/v \quad (2)$$

As the glass becomes denser the velocity of light passing through it, decreases. Hence, the higher the density of the glass, the higher the refractive index. As all the samples here, are almost equally dense, the velocities of light through them are nearly equal, which resulting in almost no variation in the n_i values. The slight increase in n_i is due to slight variations in the density of the glasses. Table 2 lists some calculated properties of the glasses.

Table 2. Some measured and calculated properties of the glasses

Sample ID	CBS	CBSD1	CBSD2	CBSD3	CBSD4	CBSD5
<i>Measured properties</i>						
Density, ρ (g.cm ⁻³)	3.4960	3.5381	3.5507	3.5608	3.5807	3.6099
Refractive index, n_i (at 532 nm)	1.6064	1.6159	1.6169	1.6173	1.6185	1.6195
<i>Calculated properties</i>						
Average molecular weight, M (g.mol ⁻¹)	100.60	100.60	100.60	100.60	100.60	100.60
Molar volume, V_m (cm ³ .mol ⁻¹)	28.78	28.43	28.33	28.25	28.09	27.87
Average molar refraction, R_m (cm ³ .mol ⁻¹)	9.9319	9.9346	9.9123	9.8893	9.8497	9.7827
Electronic polarizability, α_m (Å)	3.94	3.94	3.93	3.92	3.91	3.88
Metallization criterion, M	0.6549	0.6506	0.6501	0.6499	0.6494	0.6489
Abbe number, ν_D	59.11	58.905	59.548	58.462	59.152	59.248
Dispersive power, $1/\nu_D$	0.01691	0.016977	0.016793	0.017105	0.016905	0.016878

3.5 UV-Vis Absorption

Figure 5 shows the UV-Vis absorption spectra of the samples, which reveal that all the samples are transparent in the visible and NIR ranges. The samples containing Dy^{3+} , i.e. CBS1 to CBS5, show absorption bands at around 322, 347, 364, 388, 795 and 880 nm, which are characteristic absorption bands for Dy^{3+} that appear due to spectral transitions from ${}^6\text{H}_{15/2} \rightarrow {}^4\text{L}_{19/2}$, ${}^6\text{H}_{15/2} \rightarrow {}^4\text{M}_{15/2}$, ${}^6\text{P}_{7/2}$, ${}^6\text{H}_{15/2} \rightarrow {}^4\text{I}_{11/2}$, ${}^6\text{H}_{15/2} \rightarrow {}^4\text{I}_{13/2}$, ${}^4\text{F}_{7/2}$, ${}^6\text{H}_{15/2} \rightarrow {}^6\text{F}_{1/2}$, ${}^6\text{F}_{3/2}$, and ${}^6\text{H}_{15/2} \rightarrow {}^6\text{F}_{5/2}$, ${}^6\text{F}_{7/2}$, ${}^6\text{H}_{5/2}$ level of Dy^{3+} ions, respectively [21]. As the concentration of Dy^{3+} increases from CBS1 to CBS5, the absorption bands become increasingly prominent and sharper. As the blank glass CBS does not contain Dy^{3+} , its spectra do not exhibit any absorption bands.

3.6 Excitation Spectra

To analyze the luminescence properties as functions of the Dy^{3+} ion concentration, the excitation spectrum was recorded in the spectral range of 200–550 nm for all the samples by monitoring the emissions at 576 nm as shown in Fig. 6. The excitation bands centered at 392, 428, 453 and 472 nm are attributable to the ${}^6\text{H}_{15/2} \rightarrow {}^4\text{I}_{13/2}$, ${}^6\text{H}_{15/2} \rightarrow {}^4\text{G}_{11/2}$, ${}^6\text{H}_{15/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^6\text{H}_{15/2} \rightarrow {}^4\text{F}_{9/2}$ transitions, respectively. The broad band in the range of 230–340 nm can be attributed to the host absorption band (HAB), since the charge transfer band (CTB) of $\text{Dy}^{3+}-\text{O}^{2-}$ is located below 220 nm [23,24]. It is well-known that the wavelength corresponding to the prominent excitation band can give rise to intense emissions. In the present investigation, the excitation band centered at 453 nm was found to be most intense. Thus, the luminescence spectra should be carried out by exciting the samples with a 453 nm wavelength in order to achieve the maximum emission intensity. Due to the unavailability of a 453 nm excitation source, the emission spectra were recorded using a 447 nm (extremely close to 453 nm) laser diode [24].

3.7 Photoluminescence Spectra

Figure 7 shows the PL spectra of the samples CBS1 to CBS5. They exhibit prominent emission bands at wavelengths of 484 nm (blue), 576 nm (yellow), 664 nm (red) and 754 nm (near infrared). The major band at 576 nm is in the yellow range of the visible spectrum. It is evident from the figure that the emission intensity of the samples increases gradually from CBS1 to CBS5 i.e. with increases in Dy_2O_3 content. The inset in the figure displays the variations in emission intensity of the major band (576 nm) for all the samples. It shows gradual

increments in PL intensity with increases in the concentration of Dy^{3+} . There are no occurrence of concentration quenching for Dy^{3+} in the CBS glass matrix within the observed concentration range.

Figure 8 presents a partial energy level diagram of a Dy^{3+} ion showing the energy transfer mechanisms for the major bands in the down-conversion spectra. The 447 nm excitation wavelength promotes the electrons from the ${}^6\text{H}_{15/2}$ level to the higher ${}^4\text{I}_{15/2}$ level resulting in increased inundation in this level. The excited electrons then jump to the intermediate ${}^4\text{F}_{9/2}$ energy level through non-radiative transition. Radiative transitions take place from the ${}^4\text{F}_{9/2}$ level to various lower energy levels resulting in visible emissions from the samples. The bands at 484, 576, 664 and 754 nm correspond to the transitions ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ ($\Delta J=3$, forbidden transition), ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ ($\Delta J=2$, hypersensitive electric dipole transition), ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$ ($\Delta J=1$, magnetic dipole transition), and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{9/2}$ ($\Delta J=0$, zero-zero band, forbidden transition), ${}^6\text{F}_{11/2}$, respectively [24].

The light emitted from the luminescent samples is white in colour. Figure 9(a) shows a chromaticity chart corresponding to the light emitted from sample CBSD3 when excited at 447 nm with a diode laser source. The point “P” represents the chromaticity coordinates ($x=0.351$, $y=0.335$) of the emitted light. Figs 9(b) and 9(c) are the photographs of the luminescent sample (CBSD3) when excited at 447 nm. Both the colour coordinates and the photographs clearly show that the emitted light is white. The coordinates are very close to those of pure white light (0.333, 0.333).

Figure 10 shows the positions of the chromaticity coordinates of the light emitted by all the samples when excited at 447 nm. It can be seen that all the emitted light is white since all the coordinates lie within the white range of the chromaticity chart. Compared to the colour coordinates of all the other glasses under investigation, those of the light emitted by CBSD3 are closest to pure white light. Table 3 presents the colour coordinates of the samples and their colour temperature values. From the coordinates shown in the table, it is quite clear that the coordinates of light emitted by all the glasses are very close to each other. Since the coordinates of pure white light are $x = 0.333$, $y = 0.333$, all the samples under observation emit light that is remarkably close to pure white light. The colour temperature ranges from 3800 to 4700 K, which

is in the “cool white” range of white light. For CBSD-3 the colour temperature is 4716 K, which is comparable to daylight.

Table 3 Colour coordinates of the Dy³⁺-doped CBS glasses

Sample ID	X- axis	Y- axis	Colour Temp (K)
CBSD-1	0.376	0.364	4046
CBSD-2	0.363	0.346	4317
CBSD-3	0.351	0.335	4716
CBSD-4	0.369	0.353	4099
CBSD-5	0.392	0.389	3803

The colour of the emitted light depends on the ratio of the intensities of different emission bands. In the emission spectra of Dy³⁺-doped CBS glasses, the major bands are found at 484 and 576 nm, which are in the blue and yellow ranges of the visible spectrum, respectively. The intensity ratio of these two bands determines the colour of the emitted light. Table 4 represents the intensity ratios of these two bands for all the Dy³⁺-doped samples.

Table 4 Intensity ratio of emission bands at 484 and 576 nm

Sample ID	I ₄₈₄	I ₅₇₆	I ₅₇₆ / I ₄₈₄
CBSD1	5484	16270	2.97
CBSD2	7785	22440	2.88
CBSD3	11483	33215	2.89
CBSD4	13085	38464	2.94
CBSD5	13208	39385	2.98

It is apparent from the table that the intensity ratios are in the range of 2.88 to 2.98. The ratios are very close to each other. That is why the coordinates of the emitted colours are also very close and why all of them fall within the white range. CBSD-3 which has the closest coordinates to those of pure white light has an intensity ratio of about 2.89. Based on these observations, it can be concluded that the white light emitted by Dy³⁺-doped CBS glasses under an excitation of 447 nm will be the closest to the pure white light if and only if the intensities of the two emissions, i.e., 576 and 484 nm, obey the ratio of $I_{576}/I_{484} = 2.89$.

The photoluminescence spectra have been obtained at different laser source powers. **Figure 11** shows the PL spectra of sample CBSD-3 at various 447 nm laser powers. The

emission intensity increases gradually with increases in power. The enhancement of intensity with the raising of pump power indicates an increase in the inundation inversion, whereas all the peak positions in the PL spectra remain the same. The inset in Fig. 11 shows a plot of log of PL intensity versus a log of excitation power. Using the I versus P^K relationship (where I is intensity, P is power, and K is the order), the value of K is found to be around 1.06. The mechanism in this case is therefore on the order of one photon.

4. Conclusions

Dy³⁺-doped chloroborosilicate glasses with the composition 35.7SiO₂-25.5B₂O₃-17BaO-3.4K₂O-3.4Al₂O₃-15BaCl₂ (mol%) were prepared using a melt quenching technique; Dy³⁺ was doped in different concentrations (0.1, 0.3, 0.5, 0.7 and 1 wt% in excess). The transparent glasses were then characterized by several methods. The following conclusions can be drawn from the above results and discussion:

- The densities of the glasses are in the range of 3.5-3.6 gcm⁻³.
- The glass transition temperature (T_g) is ~610°C, as obtained from differential scanning calorimetry and dilatometry.
- The samples are found to be X-ray amorphous.
- The refractive indices are in the range of 1.60 to 1.62
- The UV-Vis-NIR absorption spectra reveal that the glasses are transparent within the entire visible range. The characteristic absorption bands of Dy³⁺ appear at 322, 347, 364, 388, 795 and 880 nm. They appear due to spectral transition from the ${}^6H_{15/2} \rightarrow {}^4L_{19/2}$, ${}^6H_{15/2} \rightarrow {}^4M_{15/2}$, ${}^6P_{7/2}$, ${}^6H_{15/2} \rightarrow {}^4I_{11/2}$, ${}^6H_{15/2} \rightarrow {}^4I_{13/2}$, ${}^4F_{7/2}$, ${}^6H_{15/2} \rightarrow {}^6F_{1/2}$, ${}^6F_{3/2}$, and ${}^6H_{15/2} \rightarrow {}^6F_{5/2}$, ${}^6F_{7/2}$, ${}^6H_{5/2}$ levels of Dy³⁺ ions, respectively.
- The excitation spectrum was recorded in the spectral range of 200–550 nm for all the samples by monitoring the emissions at 576 nm. The excitation bands centered at 392, 428, 453 and 472 nm are attributable to the ${}^6H_{15/2} \rightarrow {}^4I_{13/2}$, ${}^4G_{11/2}$, ${}^4I_{15/2}$ and ${}^4F_{9/2}$ transitions, respectively
- Under excitation of 447 nm, prominent emission bands were found at wavelengths of 484 nm (blue), 576 nm (yellow), 664 nm (red) and 754 nm (near infrared) which correspond

to the transitions ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$, ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$, ${}^4F_{9/2} \rightarrow {}^6H_{11/2}$, and ${}^4F_{9/2} \rightarrow {}^6H_{9/2}$ ${}^6F_{11/2}$, respectively. The band at 576 nm is the major one.

- PL intensity gradually increases with increases in the Dy^{3+} concentration, with no concentration quenching occurring within the experimental range.
- The emitted light from all the samples was found to be white. Their colour coordinates, all lie within the white region. The sample containing 0.5 wt% Dy_2O_3 emits white light with colour coordinates $x=0.351$, $y=0.335$ and a colour temperature of 4716 K, which appears to be the very closest to pure white light and similar to daylight.
- Variation of the excitation source power revealed the process to be single photonic.
- These white light-emitting transparent glasses promise to be enormously useful for various photonic applications, especially in WLEDs.

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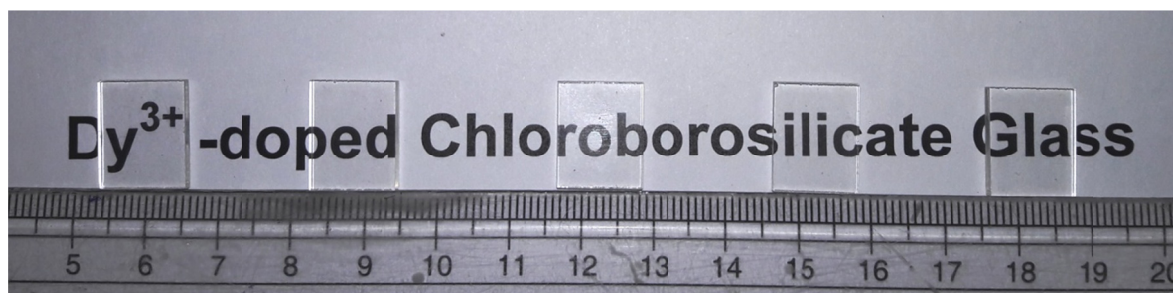


Fig. 1 Photograph of the polished samples (From left to right CBS1 to CBS5)

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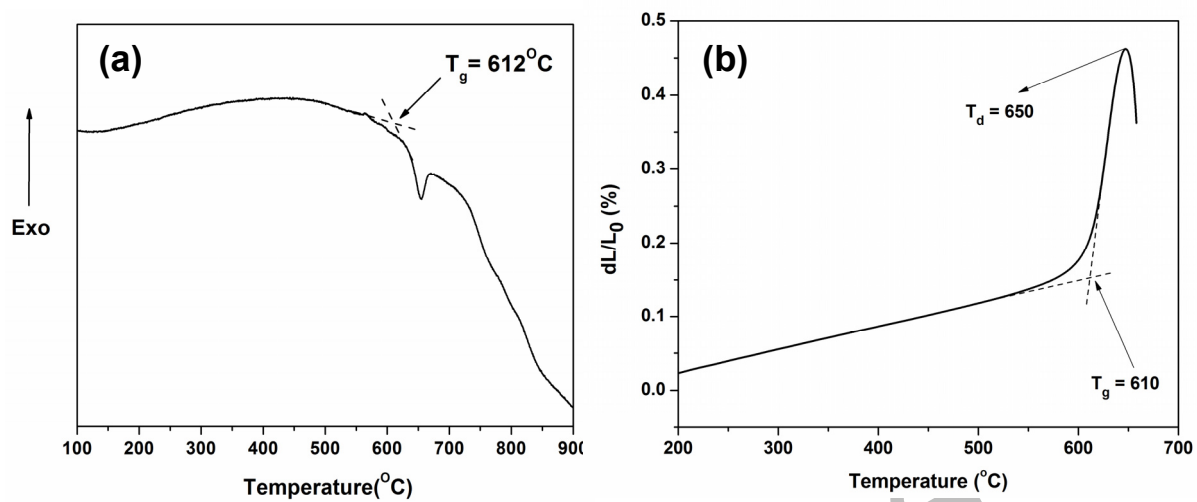


Fig. 2 (a) DSC thermogram, (b) dilatometric curve of the base glass (CBS)

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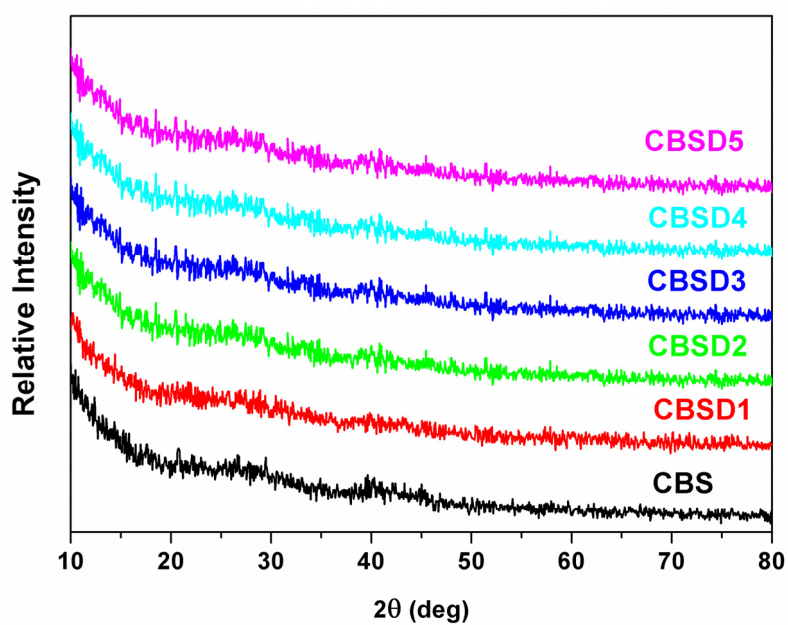


Fig. 3 XRD pattern of the samples

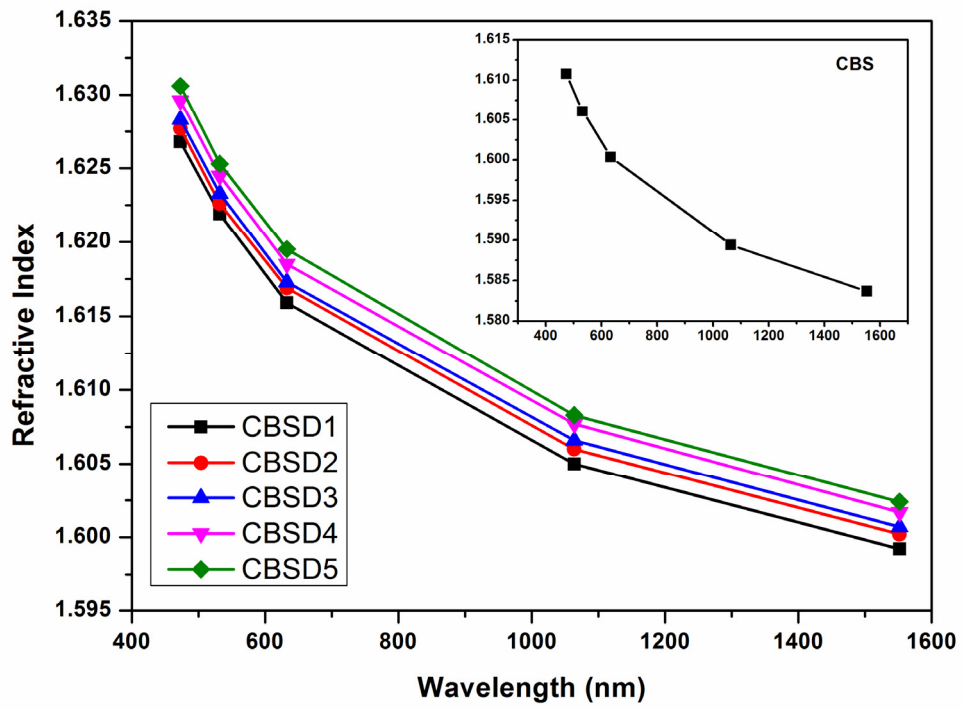


Fig. 4 Variation of refractive index of the samples as a function of wavelength; inset shows the variation of refractive index of the base glass with wavelength.

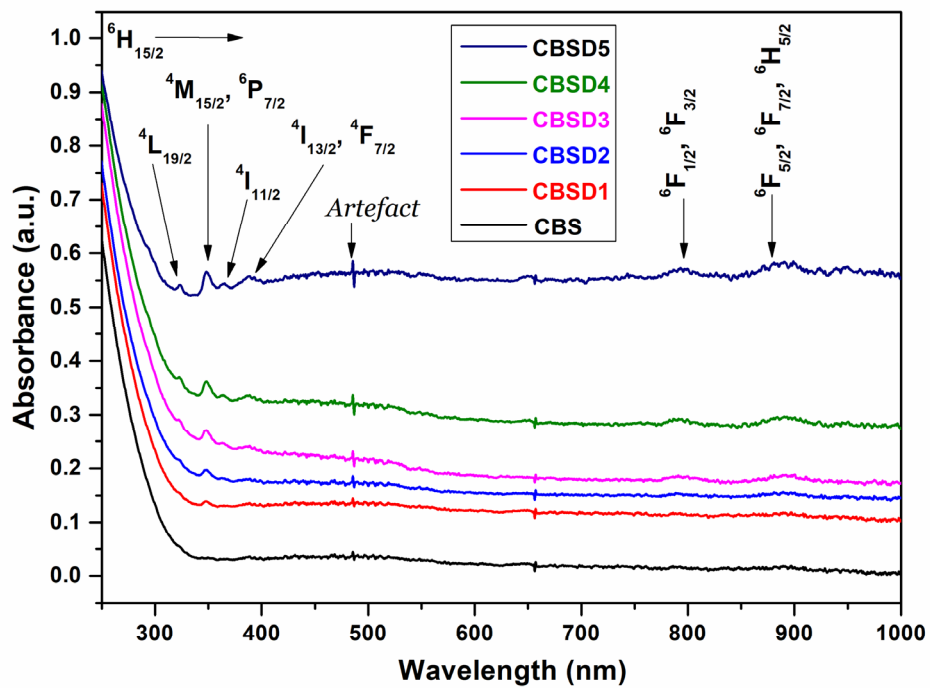


Fig. 5 UV-Vis absorption spectra of the samples

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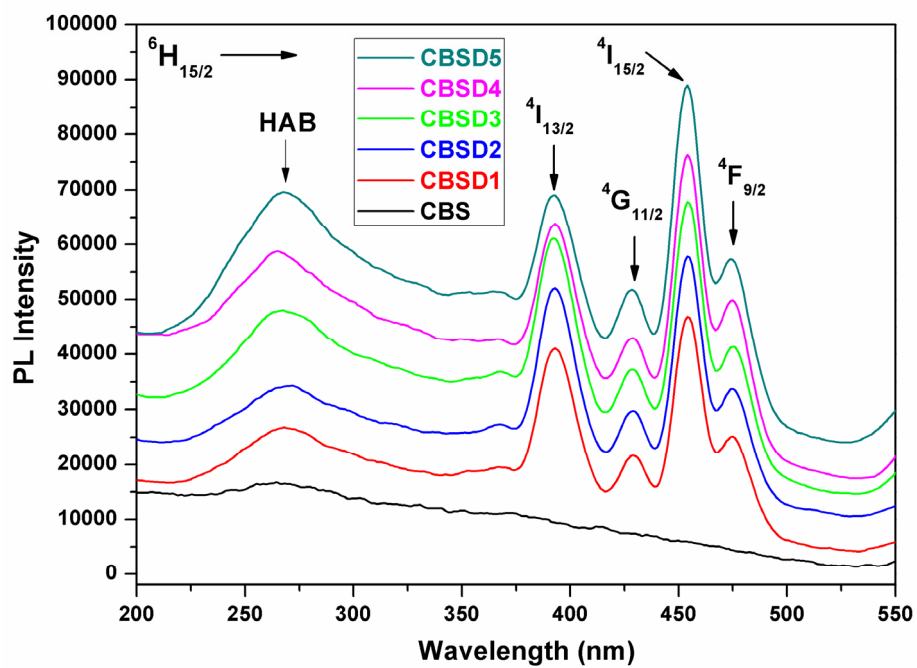


Fig. 6 Excitation spectra of the samples at excitement wavelength 576 nm

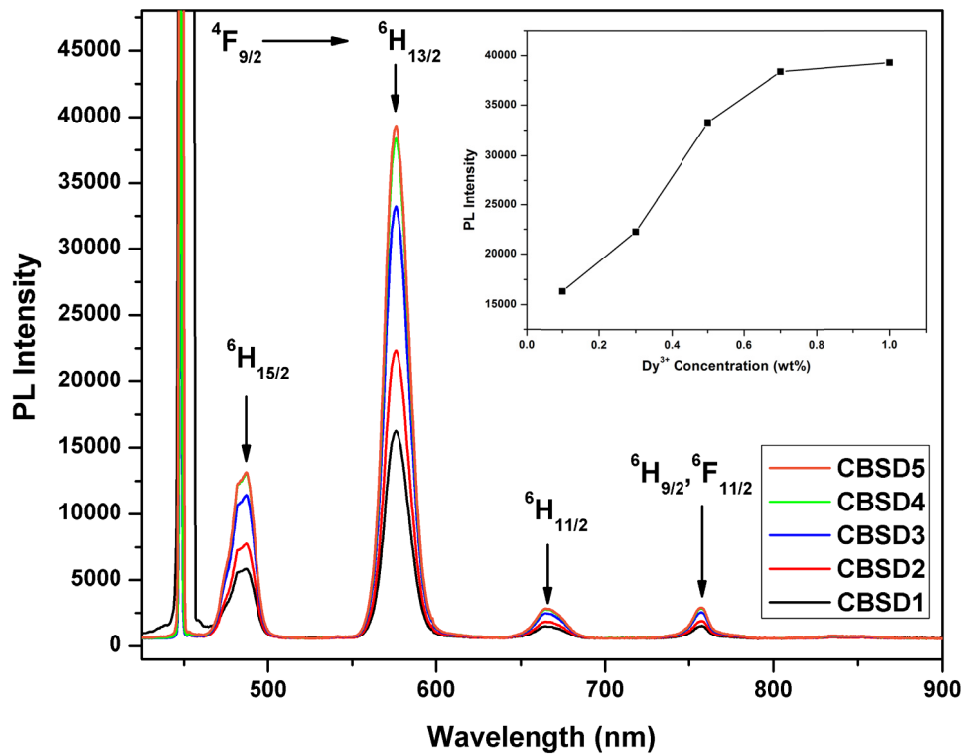


Fig. 7 PL spectra of the samples, when excited at 447 nm. Inset shows the variation of PL intensity as a function of Dy-concentration.

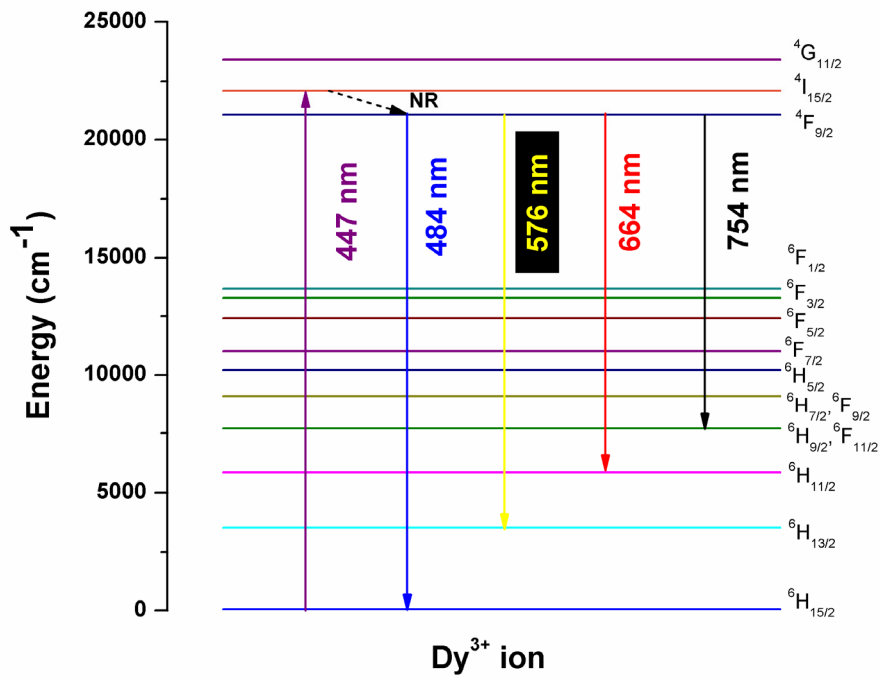


Fig. 8 Partial energy level diagram of Dy^{3+} ion showing transitions of major emission bands

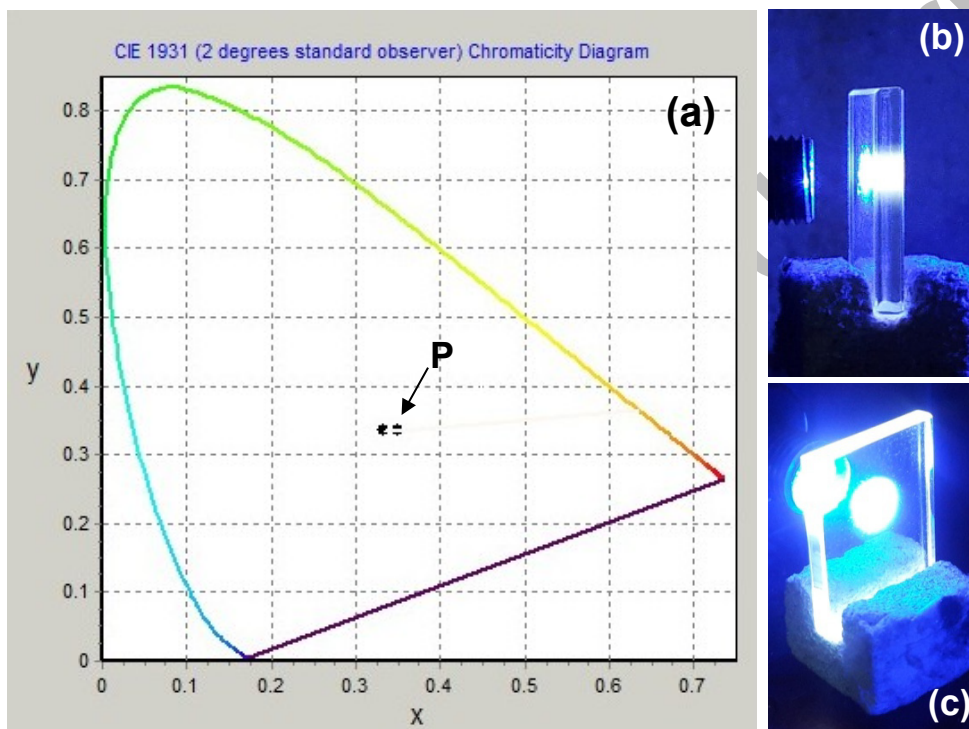


Fig. 9 (a) Chromaticity diagram corresponding to the light emitted from sample CBSD3 when excited at 447 nm with a diode laser source. The point “P” represents chromaticity coordinates ($x=0.351$, $y=0.335$) of the emitted light; (b) and (c) show the photoluminescence photograph of CBSD3, when excited at 447 nm

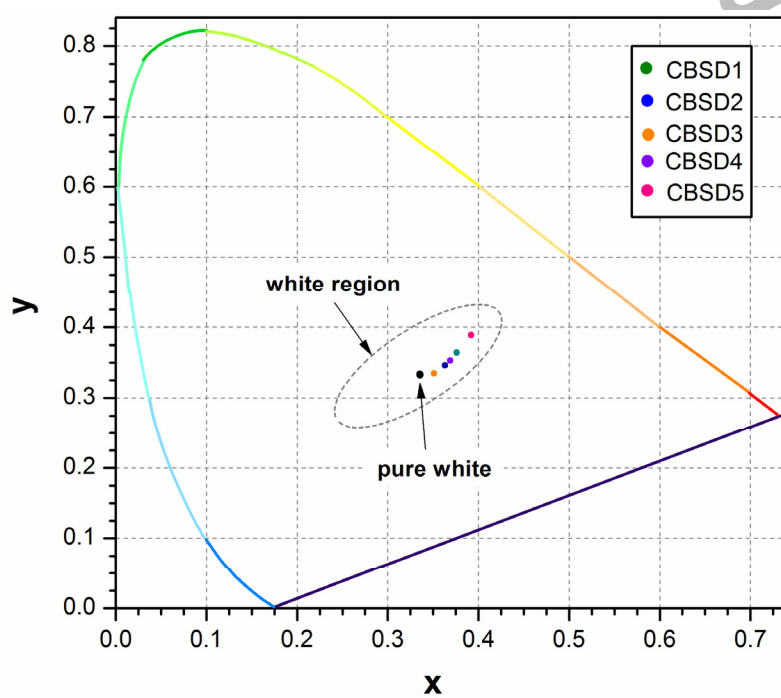


Fig. 10 Chromaticity coordinates of the emitted lights from the samples (when excited at 447 nm).

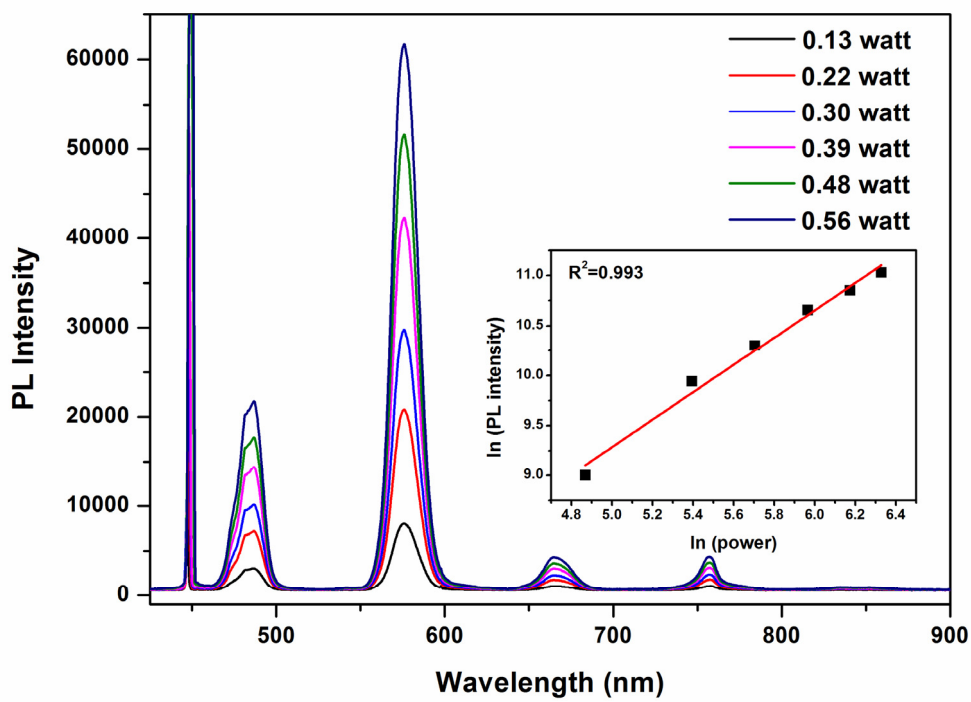


Fig. 11 Variation of PL intensity with power of the diode laser