Synthesis and photoluminescence behaviour of dysprosium doped barium bismuth borate glasses

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Dysprosium doped barium bismuth borate glasses (BBOD) with the chemical composition (75-x) H_3BO_3+ 15$BaCO_3$+ 10 Bi_2O_3 + x Dy_2O_3 (where x= 0.05, 0.1, 0.25in wt %) were prepared by melt quenching method. XRD analysis was used to confirm the amorphous nature. The prepared glass sample was characterised through optical absorption and fluorescence spectra. The presence of stretching and bending vibrational modes of borates (BO_3, BO_4 and non-bridging oxygen atoms) in the prepared glasses were explored through FTIR analysis. Thermal analysis reveals the homogenous formation of the glasses. The glass transition temperatures were also obtained from the DSC spectra. Photoluminescence spectra of the prepared glasses reveal two intense emission bands in the visible regions (blue and yellow). The x, y color chromaticity coordinates of the prepared glasses were analysed using a CIE 1931 color chromaticity diagram and it is presented.

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Keywords: Glass material, FTIR spectroscopy, Photoluminescence spectroscopy, Hruby's parameter, CIE Diagram 1931, Color purity

1. Introduction

Rare earth doped materials receive great attention due to their various photonic applications including solid state lasers, color displays, optical telecommunications, optical amplifiers, optical data storage, optical printing, remote sensors and etc. [1,2]. Glasses containing rare earth ions in various forms such as network formers, modifiers or luminescent ions receive great deal of interest for their unique optical, electrical and various other properties [3]. Borate glasses are widely investigated for several technological applications. Among the other conventional glasses like phosphate, germanate, vanadate and tellurite oxide glasses, the borate glasses are good host matrices for the rare earth ions because of their good glass forming nature, thermal stability, chemical durability and good transparency [4]. Compared to other oxides, borates possess high phonon energies (~1300 cm^{-1}) which leads to non-radiative transition. Due to this aspect we incorporate heavy metal oxides like bismuth which allow a reduction in the phonon energy and enhance possible radiative transitions. Glasses doped with trivalent rare earth ions are also considered to be promising materials for optical amplifiers [5]. Among numerous rare earth ions, dysprosium (Dy) is one of the vital role for white LED applications due to its yellow and blue intense emission bands. Dysprosium doped solid state systems are often simply excited because of their excitation spectra display many 4f-4f electronic bands.

Recently, Dy^{3+} ions were incorporated in phosphate glasses was analysed by Surendra Babu [6]. Optical absorption and photoluminescence properties of Dy^{3+}doped heavy metal borate glasses were discussed by Sasikumar et al. [7]. Structure and spectroscopy of neodymium and erbium doped lead phosphate glasses investigated by Wojciech et al. [8]. White light generation from Dy^{3+} doped tellurite glasses was demonstrated by Kamel Damak et al. [9]. Spectroscopic and photoluminescence characteristics of Dy^{3+} ions in lead containing sodium fluoroborate glasses for laser materials were studied by Madhukar Reddy et al. [10]. Luminescence quenching of Dysprosiumions in lead bismuth glasses were reported by Pisarska et al [11]. The luminescence spectra of Dy^{3+} ions in heavy metal glasses and glass ceramics were reported by Mohan Babu et al. [12], Tenabe et al [13] and Babu et al [14]. Dy^{3+} ions doped borate glasses for yellow and blue luminescence band in visible and NIR regions were reported by Kaminski et al [15, 16].

In the present work, thermal and spectroscopic properties of Dy^{3+} doped barium bismuth borate glasses were investigated and reported. The purpose of the present study is to synthesise three different concentrations of Dy^{3+} doped barium bismuth borate glasses (BBOD) and to characterize the samples using XRD, FTIR, DTA, PL etc. The studies of absorption and photoluminescence were performed in order to find the suitability of the prepared glasses for near white light emission applications and the results are discussed.

2. Experimental method

Dy^{3+} doped barium bismuth borate glasses (BBOD) were prepared by the conventional melt quenching technique. High purity analytical grade chemicals such as boric acid (H_3BO_3), barium carbonate ($BaCO_3$), bismuth oxide (Bi_2O_3) and dysprosium oxide (Dy_2O_3) were purchased from Sigma- Aldrich and were used as raw materials to prepare few glasses. Approximately 15 gm batches of chemicals were mixed and grinded in required proportions in an agate mortar. The mixtures were transferred into a porcelain crucible and were melted at 1000˚C in a high temperature furnace at ambient atmosphere. After one hour the melt was poured on a preheated brass plate mould maintained at 350˚C for 10 h to remove the thermal strain, to avoid the formation of air bubbles and to improve the mechanical strength. The samples were slowly cooled to room temperature. The glass samples with were labelled as 0.05BBOD, 0.1 BBOD and 0.25 BBOD respectively. The prepared glass samples were polished carefully before the optical measurements.

X-ray diffraction measurements were carried out using a JEOL 8530 x-ray diffractometer employing CuKα radiation source. The IR transmission spectra were measured using a Perkin-Elmer Paragon 500 FTIR spectrometer operating in the range 400 – 4000 cm^{-1} adopting the KBr pellet method. The absorption spectra were recorded between 350 to 800 nm by using Perkin–Elmer–Lambda 950 UV-Vis-NIR spectrometer with a spectral resolution of ±0.1 nm. The glass sample (5 mg) was heated in a platinum pan at the rate of 10 ˚C/min in the temperature range 30-1200 ˚C and their thermal behaviour (glass transition temperature T_g, glass crystallization temperature T_c and melting temperature T_m) was measured by DSC thermal analyser SDT Q600 V8.3 Build 101. The photoluminescence spectra were recorded using a Perkin-Elmer LS55 spectrometer in the wavelength of 500 to 700 nm with a spectral resolution of ±1.0 nm at room temperature.

3. Results and discussions

3.1. Structural analysis

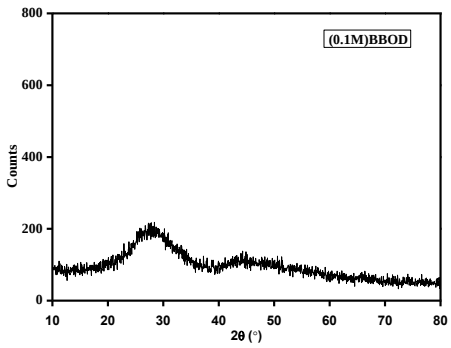

Fig. 1. XRD pattern of the Dy^{3+} doped Barium Bismuth Borate glass

The XRD pattern of the Dy^{3+} doped 0.1 BBOD glass shown in Fig. 1. This exhibits broad diffused scattering at lower angles suggesting the long range structural disorder and confirms the amorphous nature of the prepared glasses.

3.2. FTIR analysis

Infrared spectroscopy is used to identify the presence functional groups in the prepared glasses. FTIR spectra of the Dy^{3+} doped barium bismuth borate glasses were recorded in the wave number region 400 – 4000 cm^{-1} and the same is shown in Fig. 2. The percentage transmission of the radiation is found to be maximum between 650 and 3000 cm^{-1} for all the glasses. The weak shoulder around 455 cm^{-1} is assigned to isolated diborate group (BO_2). The absorption around 714 cm^{-1} is assigned to the oxygen bridges between two trigonal boron atoms and is attributed to B-O-B bending vibrations. The peak positions around 1010 cm^{-1} confirm the stretching vibrations of BO_4 group. The broad band at 1410 cm^{-1} in the spectra is due to the B-O asymmetric stretching of BO_3 units. The peak around 3662 cm^{-1} is attributed to the fundamental stretching of the O-H groups and the peaks around 2852 cm^{-1}, 2934 cm^{-1} reveal the presence of hydrogen bonding. [18-21]. The characteristic active modes of vibrations of borate network in all these glasses are similar to other borate based glasses reported earlier [22,23].

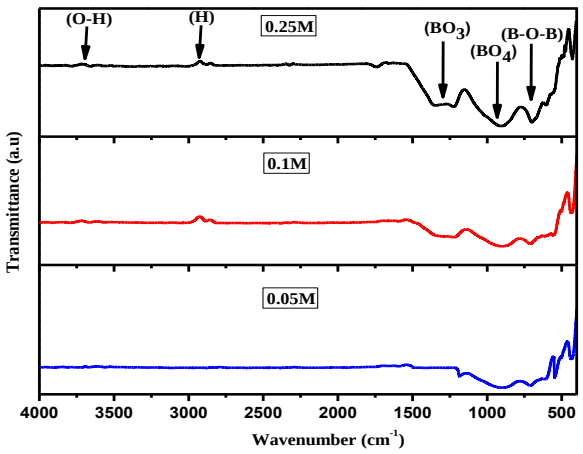

Fig. 2. Infrared spectra of the Dy^{3+} doped Barium Bismuth Borate glass

3.3. Thermal analysis

DSC analysis was carried out in order to establish the thermal stability of the prepared glass and is shown in Fig. 3. Through the DSC thermograms, the glass transition temperature (T_g), crystallization temperature (T_c) and the melting temperature (T_m) were identified.

$$\text{Glass stability factor (S)} = (T_c - T_g) \quad (1)$$

Hruby's parameter (H_R) $= (T_c-T_g)/(T_m-T_c)$ (2)

These values calculated from the measured values of T_g, T_c, and T_m and the results were presented in Table 1. The prepared glass has high stability factor ($T_c - T_g$) and minimum temperature interval between crystallization& melting is determined which creates the best candidate for optical fiber fabrication technology [24] as there is a reduced chance of crystallization. The value of the Hruby's parameter is high and it leads the large glass forming tendency.

Table 1. Glass transition temperature (T_g), glass crystallization temperature (T_c) and melting temperature (T_m) and stability factor (S), Hruby's parameter (H_R) of the prepared Dy^{3+} doped barium bismuth borate glass

Sample	T_g (℃)	T_c (℃)	T_m (℃)	$S = (T_c - T_g)$ (℃)	$H_R = \frac{(T_c - T_g)}{(T_m - T_c)}$
0.1BBOD	514	588	940	74	0.21

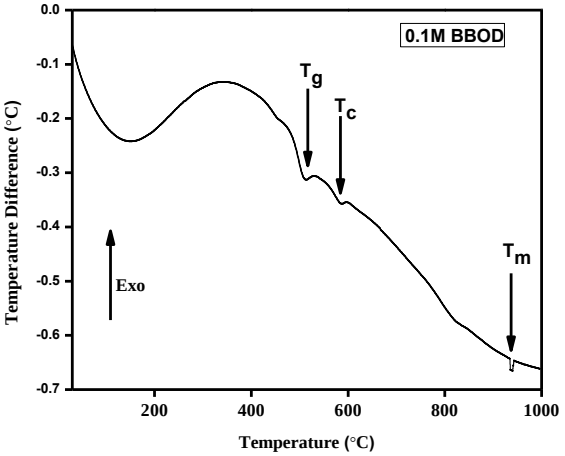

Fig. 3. DSC of the Dy^{3+} doped Barium Bismuth Borate glass

3.4. Absorption spectra

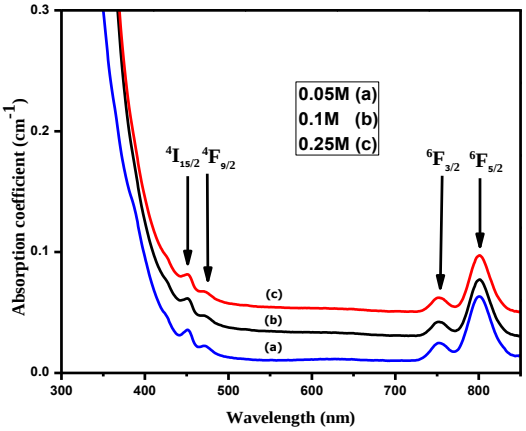

Fig. 4. Absorption spectrum of the Dy^{3+} doped Barium Bismuth Borate glass

Optical absorption spectrum of the Dy^{3+} doped barium bismuth borate glasses were recorded in the visible region and is shown in Fig. 4. The spectrum exhibits four absorptions centered at 449, 469,751 and 801nm that originates due to the electric dipole (ED) transition from the $^6H_{15/2}$ ground state to the various excited states of dysprosium ion such as $^4I_{15/2}$, $^4F_{9/2}$, $^6F_{3/2}$ and $^6F_{5/2}$ respectively. The observed band positions are found to be same irrespective of the change in the glass compositions and the band assignments were made based on the reported literature [25].

3.5. Excitation and emission spectra

Fig. 5 shows the excitation spectra of the Dy^{3+} doped barium bismuth borate glasses by fixing the emission wavelength at 595 nm. The excitation spectra were recorded in the spectral region 300-500 nm. Six bands that correspond to the transitions from $^6H_{15/2}$ to different excited states, $^6P_{7/2}$ (350 nm), $^6P_{5/2}$ (365 nm), $^4I_{13/2}$ (387 nm), $^4G_{11/2}$ (426 nm), $^4I_{15/2}$ (453 nm) and $^4F_{9/2}$ (471 nm) were observed in the spectra for all the glasses.

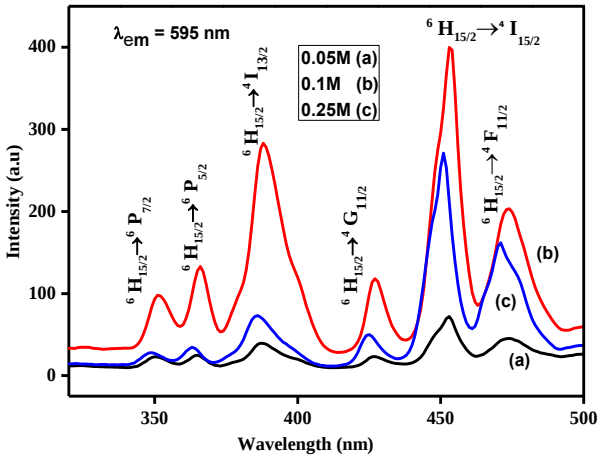

Fig. 5. Excitation spectra of the Dy^{3+} doped Barium Bismuth Borate glasses

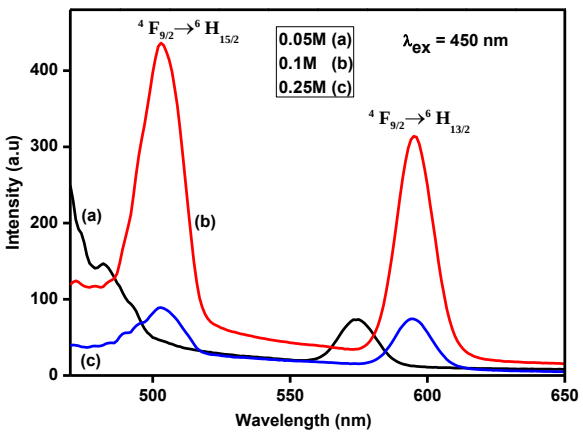

Fig. 6. Emission spectra of the Dy^{3+} doped Barium Bismuth Borate glasses

In the present investigation, the luminescence spectra were carried out by exciting the samples with 450 nm radiation. The emission spectra were recorded in the spectral region of 450-650 nm for all Dy^{3+} doped glasses and are shown in Fig. 6 and Fig. 6.1 shows the energy level scheme of excitation and emission transitions. The spectra exhibit two strong luminescence bands at $^4F_{9/2} \rightarrow {}^6H_{15/2}$(blue) and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (yellow). The shapes of the emission peaks are similar in all the glass matrices except for a small variation in the intensity of the emission transition.

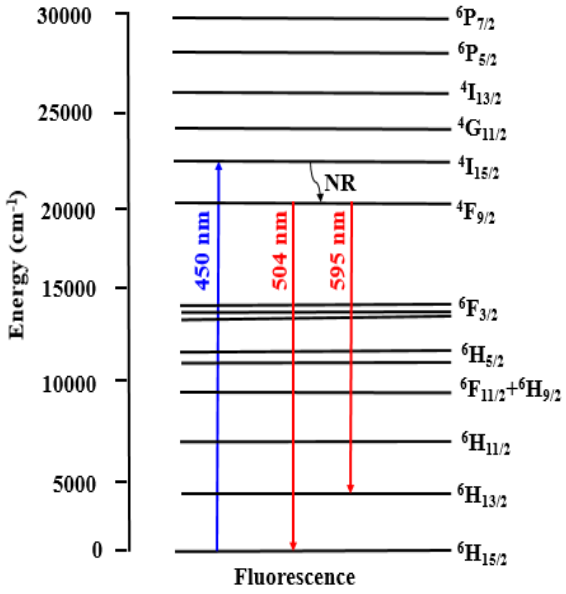

Fig. 7. Energy level of the Dy^{3+} doped Barium Bismuth Borate glasses

3.6. CIE Chromaticity analysis

The colour of any light source can be described by three variables $\bar{x}(\lambda)$,$\bar{y}(\lambda)$ and $\bar{z}(\lambda)$ (colour matching functions), which are dimensionless quantities [26]. For a given power-spectral intensity P (λ), the degree of stimulation required to match the color P (λ) is given by

$$X = \int_{\lambda} \bar{x}(\lambda)P(\lambda)d\lambda \quad (3)$$

$$Y = \int_{\lambda} \bar{y}(\lambda)P(\lambda)d\lambda \quad (4)$$

$$Z = \int_{\lambda} \bar{z}(\lambda)P(\lambda)d\lambda \quad (5)$$

Where X, Y and Z are the tristimulus values which give stimulation (i.e. power) for each of the three primary red, green and blue colors needed to match the color P(λ).The chromaticity coordinates x and y are calculated from the tristimulus values according to the following equations [27]

$$x = \frac{X}{X+Y+Z} \quad (6)$$

$$y = \frac{Y}{X+Y+Z} \quad (7)$$

The values of the color chromaticity coordinates (x, y) are found to be (0.263, 0.417), (0.281, 0.363) and (0.278, 0.376) corresponding to the 0.05BBOD, 0.1BBOD glasses 0.25 BBOD glasses respectively. Fig. 7 represents the CIE chromaticity diagram of the glasses and it is observed from the figure that the x, y values of all the glass samples fall in the near white region. Hence, it is suggested that the prepared dysprosium doped barium bismuth borate glasses are suitable for laser applications, light emitting diodes and display devices.

3.7. Color purity

The color purity or color saturation of a particular dominant color in a source is the distance in the chromaticity diagram between the emission color coordinates and the coordinates of equal energy point, divided by distance between the equal point and the dominant wavelength point. Thus the color purity is given by

$$\text{Color purity} = \frac{\sqrt{(x-x_{ee})^2+(y-y_{ee})^2}}{\sqrt{(x_d-x_{ee})^2+(y_d-y_{ee})^2}} \quad (8)$$

Where (x, y), (x_{ee}, y_{ee}) and (x_d, y_d) are the chromaticity coordinates of the emission light, equal energy point and dominant wavelength points, respectively.

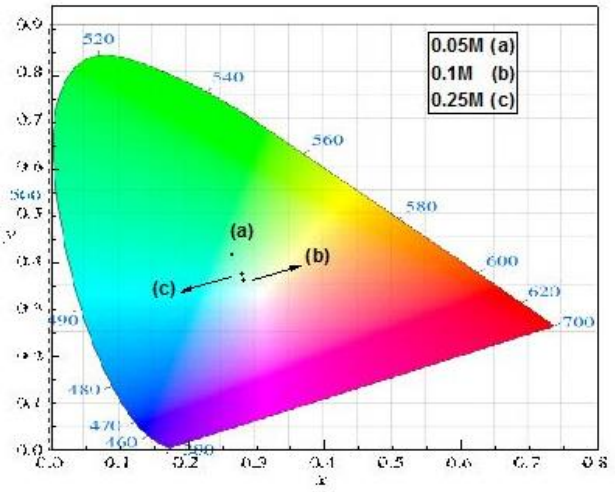

Fig. 8. CIE Chromaticity diagram of the Dy^{3+} doped Barium Bismuth Borate glasses

From Fig. 8 for all the Dy^{3+} doped barium bismuth borate glasses, the color coordinates are located just aside of the pure white color located at the centre of the diagram. This implies that the light emitted by Dy^{3+} ions embedded in the BBOD glasses is not perfect white light but possess the dominant wavelength deviating from its white light emitting property. The dominant wavelength is determined by drawing a straight line from pure white

light coordinates i.e., equal energy point (0.33, 0.33) to the color coordinates of Dy^{3+} ions emission in glasses. The color purity of three glasses have the value of (20.39%), (52.00%), (30.82%). Among the three glasses 0.1BBOD glass possess the high color purity. The color purity at 595 nm wavelength was found to be 0.5212 (52%).

4. Conclusion

The paper elucidates the method of preparing Dysprosium doped barium bismuth borate (BBOD) glasses among with a detailed discussion on structural, thermal and optical properties of Dy^{3+} ions in the barium bismuth borate glasses. XRD pattern confirms the amorphous nature of the prepared glasses. FTIR spectra reveal the presence of O-H vibrations, B-O bond of trigonal BO_3 units and the vibrations of B-O-B linkages in the borate network. The DSC curves have been used to study the thermal properties like glass stability factor and Hruby's parameter. The color chromaticity coordinates of the present glasses are found to lie in the near white light region of the CIE 1931 chromaticity diagram making them potential candidates for white LED applications.

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