Effects of BaO and Bi$_2$O$_3$ on the optical and luminescence properties of Dy$^{3+}$ doped borophosphate glasses

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Abstract. Barium borophosphate glass and bismuth borophosphate glass doped with 1 mol% dysprosium oxide were synthesized by melt-quenching technique at 1200 ºC for 3 hrs. Both glasses were studied optical and luminescence properties to evaluate their potential for using as luminescence materials. The absorption spectra in the region of ultraviolet, visible and near-infrared from 300 to 2000 nm wavelength were investigated. The luminescence spectra showed the strong emission band at 573 nm ($^4$F$_{9/2}$ $\rightarrow$ $^4$H$_{13/2}$) under 350 nm excitation wavelength, which the shapes of the emission bands are similar in both glasses. The optical absorption and luminescence intensity of barium borophosphate glass are higher than bismuth borophosphate glass. Also, it is observed that the direct and indirect bandgap values of barium borophosphate glass are larger than bismuth borophosphate glass.

1. Introduction
Glasses are among the most suitable inorganic materials for the development of advanced photonic devices due to their high transparent, high doping capability, cheap production cost and ease of manufacture in different sizes and shapes [1,2]. Phosphate glasses have attracted considerable attention and have been investigated extensively due to high transparency and low melting temperature [3,4]. However, phosphate glasses has poor chemical durability and high hygroscopic nature due to the presence of hygroscopic P-O-P bonds, which often limits their usefulness [5]. But this problem can be solved by adding modifier oxides (Na$_2$O, Li$_2$O, BaO, etc.) or heavy metal oxides (Al$_2$O$_3$, TiO$_2$, Bi$_2$O$_3$, etc.) to phosphate glass network. The addition of these oxides results in the conversion of three dimensional structure into linear chains thus leading to the cleavage of P-O-P linkages with the formation of (Al, Ba or Bi)-O-P bonds [6-9]. Normally, Bi$_2$O$_3$ are known as both network forming and network modifying positions in oxide glasses which lead to the formation of a stable Bi-O-P bond can be improve the chemical durability of phosphate glasses. Furthermore, Bi$_2$O$_3$ containing glasses reduce phonon energy and result into an increase in the quantum efficiency of luminescence properties [10]. The addition of BaO in phosphate glasses is often used to modify for low field strength cations where BaO improves the mechanical properties which are prerequisite for a good laser glass [11,12]. It is well known that, the combination of B$_2$O$_3$ and P$_2$O$_5$ gives a novel and very efficient borophosphate glasses for optically active ions because of their high thermal stability, ultraviolet transmission, optical characteristic and good chemical stability [13].
In recent years, luminescence properties of rare earth (RE) ions doped glasses materials have extensively been investigated for multiple photonic devices including lasers [14,15], white light emitting diodes [16,17], luminescence materials. [18], optical amplifiers [19,20] and radiation detector [21,22]. Particularly, trivalent dysprosium (Dy$^{3+}$) doped glasses have been widely adopted for white light emitting diodes due to its good emission in white region with high luminescence efficiency. Dy$^{3+}$ doped glasses typically emitting two intense emissions in the blue ($^4F_{9/2} \rightarrow ^6H_{15/2}$) at 485 nm and yellow ($^4F_{9/2} \rightarrow ^6H_{13/2}$) at 573 nm, which combining the blue and yellow emission light, the white light can be generated [23,24]. Therefore, Dy$^{3+}$ doped glasses were study and developed widely to reach the best glass for solid-state lighting applications, especially for white LEDs such as Na$_2$O-ZnO-Al$_2$O$_3$-B$_2$O$_3$-Dy$_2$O$_3$ [16], PbO- Al$_2$O$_3$- B$_2$O$_3$-Dy$_2$O$_3$ [17], TeO$_2$-WO$_3$-PbO-ZnO-Dy$_2$O$_3$ [23] and Na$_2$O-PbO-Al$_2$O$_3$-B$_2$O$_3$–SiO$_2$-Dy$_2$O$_3$ [24].

In the present study, the effects of BaO and Bi$_2$O$_3$ on the various properties of Dy$^{3+}$ doped borophosphate glasses were investigated, with the aim to improve its optical and luminescence properties.

2. Experimental method

The chemical composition and labels of Dy$^{3+}$ doped glasses are presented in Table 1. The melt quenching technique was employed to prepare glasses samples using the Bi$_2$O$_3$, BaCO$_3$, H$_2$BO$_3$, NH$_4$H$_2$PO$_4$ and Dy$_2$O$_3$ chemicals as starting materials. The chemicals of BiBP$^+$d and BaBP$^+$d glasses were melted at 1,200 °C for 3 hrs. in an electric muffle furnace. Then, the melt glasses were poured into a pre-heated graphite mold and annealed in an annealing furnace at 500 °C for 3 hrs. before cooled down at room temperature.

Table 1. Chemical composition and labels of Dy$^{3+}$ doped glasses.

| Glass labels | Chemical composition of glasses |
|--------------|--------------------------------|
| BiBP$^+$d    | 25Bi$_2$O$_3$:5B$_2$O$_3$:69P$_2$O$_5$:1Dy$_2$O$_3$ |
| BaBP$^+$d    | 25BaO:5B$_2$O$_3$:69P$_2$O$_5$:1Dy$_2$O$_3$ |

The optical absorption spectra of glasses were recorded at room temperature using UV-Vis-NIR spectrophotometer (Shimadzu, UV-3600). The excitation and emission spectra were monitored with fluorescence spectrophotometer (Agilent Technologies, Cary Eclipse) using xenon lamp as a light source. CIE 1931 chromaticity diagram was used to determine color of the emission light obtained from the emission spectra [24].

The density measurement was done under Archimedes principle using a 4-digit sensitive microbalance (AND, HR-200). The obtained density values were brought to calculate the molar volume of glass samples. The refractive index of the glass samples was measured by Abbe refractometer (ATAGO) with a sodium vapor lamp as a light source (589.3 nm) and using mono bromonaphthalene (C$_{10}$H$_4$Br) as an adhesive liquid. The absorption coefficient, ($\alpha$), of glass spectrum was calculated using the equation:

$$\alpha = \frac{1}{d} \ln \frac{I_0}{I_t}$$  \hspace{1cm} (1)

where $d$ is the thickness of sample (cm), $I_0$ and $I_t$ are the incident and transmitted radiation beam. The optical band gap of glasses was evaluated from:

$$a\hbar\nu = a_0 (\hbar\nu - E_g)^n$$  \hspace{1cm} (2)

where $a_0$ is a constant, $\hbar\nu$ is the incident photon energy and $n$ is the index with different values ($n = 2$, 3, 1/2 and 2/3 corresponding to indirect allowed, indirect forbidden, direct allowed and direct forbidden, respectively).
3. Result and discussion

3.1. Physical properties

The various physical properties of glass samples are presented in Table 2. It is obvious that the density, average molecular weight and refractive index of BiBPDy glass has higher than BaBPDy glass because of higher molecular weight of Bi$_2$O$_3$ (465.9589 g/mol) in BiBPDy glass than BaO (153.3264 g/mol) in BaBPDy glass [25]. Similarly, the refractive index of BiBPDy glass is greater than that of the BaBPDy glass, which is due to the higher density of the Bi$_2$O$_3$ than BaO compounds [26]. In addition, the molar volume of BiBPDy glass is also higher than BaBPDy glass. This is because the three oxygen atoms of Bi$_2$O$_3$ in BiBPDy glass occupied more space than the one oxygen atom of BaO ion in BaBPDy glass cause the increasing of the molar volume. These results identical to previous reported work [26].

### Table 2. Physical properties of glass samples.

| Properties                  | BiBPDy          | BaBPDy          |
|-----------------------------|-----------------|-----------------|
| Density, $\rho$ (g/cm$^3$)  | 3.9867±0.0032   | 3.0787±0.0023   |
| Refractive index, $n$       | 1.6562±0.0003   | 1.5506±0.0005   |
| Molar volume, $V_{m}$ (cm$^3$/mol) | 55.5955       | 46.6055        |
| Average molecular weight, $M_T$ (g/mol) | 221.6424     | 143.4843       |

3.2. Optical absorption spectra

The optical absorption spectra of Dy$^{3+}$ doped bismuth and barium borophosphate glasses, recorded in the wavelength range of 300-2000 nm, are shown in Figure 2. As seen in Figure 2, the absorption spectra of BiBPDy glass consist six absorption bands while that of BaBPDy glass consist of nine
absorption bands, corresponding to the transitions from $^5\text{H}_{15/2} \rightarrow ^4\text{F}_{7/2}$ (387 nm), $^4\text{G}_{11/2}$ (425 nm), $^4\text{I}_{15/2}$ (451 nm), $^6\text{F}_{3/2}$ (757 nm), $^6\text{F}_{5/2}$ (804 nm), $^6\text{F}_{7/2}$ (901 nm), $^6\text{H}_{3/2}$ (1095 nm), $^6\text{F}_{11/2}$ (1277 nm) and $^6\text{H}_{11/2}$ (1685 nm) [27]. It is clearly observed that, only the peak at 387, 425 and 451 nm were not observed in the absorption spectrum of BiBPDy glass system, which is attributed to the absorption edge of BiBPDy glass was near 400 nm. Generally, in the bismuth glass, a strong absorption is observed in the UV region at about 400 nm, which is identical to previous reported work [25,26,28,29].

### 3.3. Optical band gap

The optical band gap is an important parameter in the field of photonics which gives information about the electronic structure of amorphous materials for predicting energy effects and energy gaps in inorganic solids. The optical band gap can be evaluated from the fundamental absorption edges of the absorption spectral through the direct and indirect allowed transitions. The calculated optical band gap for the direct ($n = 2$) and indirect ($n = 1/2$) transition of BiBPDy and BaBPDy glasses are presented in Table 3 and Figure 3. From Table 3, it is clear that the cut-off wavelength observed that 367 nm for BiBPDy glass, which is found to be shifted towards the longer wavelength side indicating that BiBPDy glass show lower optical band gap compared with BaBPDy glass. The smaller of optical band gap might due to the higher level of disorder in the glass matrix which results in more space and extension of the localized states within the optical energy band gap. The values of optical band gap in the present study are in good agreement with the available experimental data [26].

| Glass labels | Cut-off wavelength (nm) | Direct band gap (eV) | Indirect band gap (eV) |
|--------------|-------------------------|----------------------|-----------------------|
| BiBPDy       | 367                     | 2.577                | 1.993                 |
| BaBPDy       | 325                     | 3.517                | 3.241                 |

3.4. Excitation and emission spectra

The excitation spectra of BiBPDy and BaBPDy glasses have been recorded by emission wavelength at 573 nm as shown in Figure. 4(a). Totally nine excitation bands at 298, 325, 338, 350, 364, 387, 426, 452 and 473 nm are observed which are assigned to $^7\text{H}_{15/2} \rightarrow ^4\text{H}_{13/2}$, $^4\text{I}_{5/2}$, $^4\text{F}_{9/2}$, $^4\text{H}_{3/2}$, $^4\text{F}_{7/2}$, $^4\text{P}_{5/2}$, $^4\text{G}_{11/2}$, $^4\text{I}_{15/2}$ and $^4\text{F}_{9/2}$ transition, respectively [27]. Among these transitions, the $^3\text{H}_{15/2} \rightarrow ^6\text{P}_{7/2}$ (573 nm) transition
is mostly significant and its transition wavelength can be used for measuring the emission spectra of BiBPDy and BaBPDy glasses.

![Excitation (a) and emission (b) spectra of glass samples.](image)

Figure 4(b) shows the emission spectra of glass samples recorded under the 393 nm excitation wavelength. Two strong bands at 482 nm (blue) and 573 nm (yellow) and a weak band at 662 nm (red) are identified from the emission spectra, corresponding to \(F_{9/2} \rightarrow H_{15/2}\), \(F_{9/2} \rightarrow H_{13/2}\), \(F_{9/2} \rightarrow H_{11/2}\) and \(F_{9/2} \rightarrow H_{9/2}\) transitions, similar to those reports in Dy\(^{3+}\) doped glasses [30,31]. It is obvious that the emission spectrum of BaBPDy glass shows higher emission intensity than BiBPDy glass. Generally, the intensity of \(F_{9/2} \rightarrow H_{13/2}\) (magnetic dipole transition) does not depend on the local crystal field environment of the constituent atoms in glass matrices. Whereas, the intensity of \(F_{9/2} \rightarrow H_{11/2}\) transition (electric dipole transition) depends on local environment, this transition is called as the hypersensitive emission transition. Therefore, greater the intensity of \(F_{9/2} \rightarrow H_{11/2}\) transition, suggest the pronounced nature of asymmetry effects in the host matrix. Accordingly, the BaBPDy glass possess more asymmetry of the local environment around Dy\(^{3+}\) ion than BiBPDy glass and the results the emission intensity of BaBPDy glass is higher than BiBPDy glass [26,32,33,34].

3.5. CIE 1931 chromaticity coordinates

The chromaticity coordinates of emission spectra in the CIE 1931 chromaticity diagram framework were used to evaluate color of emitted light sensed by human eyes perceives. The color coordinate \((x, y)\) of BiBPDy and BaBPDy glasses were found to be \((x = 0.388, y = 0.434)\) and \((x = 0.374, y = 0.424)\), respectively, which fall in the white light region of CIE 1931 chromaticity diagram as presented in Figure. 5(a). The photograph of the white light emission of the glass samples under excited by 365 nm ultraviolet lamp, to confirm white light emitting, are also shown in Figure. 5(b). It is observed from Figure. 5 that, the CIE coordinates of BiBPDy glass deviated towards green-yellow region, this may be due to normally the color of BiBPDy glass is shown yellow color. However, the \((x, y)\) color chromaticity coordinates values of the BiBPDy and BaBPDy glasses are comparable with other Dy\(^{3+}\) doped NPABSDy [24], KFPDy [31], LGBiBDy [35] and YCaSBDy [36] glasses. These results affirm that BiBPDy and BaBPDy glasses are promising materials for producing white light emission.
Figure 5. The CIE 1931 diagram of BiBPDy and BaBPDy glasses, (b) white emission excited by 365 nm UV lamp of BiBPDy and BaBPDy glasses.

4. Conclusions
The physical, optical and luminescence properties of BaBPDy glass and BiBPDy doped with 1 mol% dysprosium oxide were measured in order to examine the effect of BaO and Bi₂O₃ for using as luminescence materials. From this research, the absorption bands of BaBPDy glass were clearly observed in the UV–Vis–NIR regions, while BiBPDy glass were observed in the Vis–NIR regions due to the absorption edge of BiBPDy glass was near 400 nm. It is also observed that the direct and indirect band gap values of BiBPDy glass are smaller than BaBPDy glass. The emission spectra \( (\lambda_{ex}=350\,\text{nm}) \) of both glasses shows the sharpest peak centered at 573 nm \( (4\,\text{F}_{9/2} \rightarrow 6\,\text{H}_{13/2} \text{transition}) \). The BaBPDy glass has higher emission intensity than BiBPDy glass, because the BaBPDy glass possess more asymmetry of the local environment of the Dy³⁺ ion than BiBPDy glass. From CIE 1931 chromaticity coordinate, both BiBPDy and BaBPDy glasses can emit the white light. Preliminary studies show that BiBPDy and BaBPDy glasses perform high potential for using as luminescence materials for white LEDs. Furthermore, the BaBPDy glass provides higher luminescence potential than the BiBPDy glass.

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