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Invited Paper

Photoluminescence Study of Bismuth Borophosphate Glasses Doped with Dy^{3+} Ions

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Abstract. Bismuth borophosphate (Bi_2O_3-B_2O_3-P_2O_5) glasses doped with Dy^{3+} ions were produced by melt quenching procedure. The doping concentration of the Dy^{3+} was varied from 0.2 mol% to 1.0 mol%. The obtained glasses were characterized through the optical absorption and photoluminescence (PL) spectral measurements. The emission spectra corresponding to the Dy^{3+}: $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (483 nm), $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (573 nm), $^4F_{9/2} \rightarrow {}^6H_{11/2}$ (663 nm) and $^4F_{9/2} \rightarrow {}^6H_{9/2}$ (753 nm) transitions were obtained under excited wavelength at 350 nm. The photoluminescence intensities of all glasses are comparable and the strongest intensity peak at 573 nm was obtained with 0.8 mol% Dy^{3+} ions. In order to identify the emission color of the prepared glasses, the emission intensities were analyzed using the 1931 CIE chromatic color coordinates.

1. Introduction

Normally, phosphate glasses have linked PO_4 structural units with covalent bonding oxygen that affect to the some unique physical properties, which are better than borate and silicate glasses [1]. This glass has been of large interest for a variety of technological applications due to the unique properties such as high thermal expansion coefficient, low viscosity, low chemical durability, UV transmission or electrical conduction [2-4]. However, the pure phosphate network is not stable because of its hydroscopic nature. The addition of B_2O_3 to a phosphate network improves the chemical durability as well as the thermal and mechanical stability of pure phosphate glass [5]. The agglomeration of B_2O_3 into metaphosphate glasses produces the new linkages between phosphate chains through P–O–B bonds [6]. There have been some studies on borophosphate glasses with various network modifiers that have been developed for widespread applications, including hermetic sealing materials [7-9], fast ion conductors and solid state batteries [10]. Glasses based on Bi_2O_3 show the interesting physical properties such as high density, high linear and non-linear refractive index enabling their extensive applications in optical and optoelectronics [11].

The luminescence properties of the trivalent lanthanide ions doped materials have been the interested applications in various fields such as lasers, optical amplifiers, temperature sensors, etc. The trivalent lanthanide ions can emit different colored light depending on the concentration of rare earth (RE) ions as well as surrounding environment. At present, a good deal of research has been focused on the possible applications of rare earth ions doped glasses in the fabrication of white LEDs [12]. Dy^{3+} is one of the important rare earth ions which play a major role in the production of different types of light-emitting materials. This ion possesses intense emission at blue and yellow regions, which are associated with the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions, respectively [13].

In the present work, bismuth borophosphate (Bi_2O_3-B_2O_3-P_2O_5) glasses doped with Dy^{3+} ions were prepared by the melting and quenching process. The optical absorption and photoluminescence properties of the obtained glasses were studied using a spectrophotometer at room temperature. The

1931 CIE chromatic color coordinates was also investigated using emission data to confirm the white emission from glasses.

2. Experiments

Glass preparation. Bismuth borophosphate glass doped with Dy^{3+} ions (BiBPDy) in composition of $25Bi_2O_3 : 5B_2O_3 : (70\text{-}x)P_2O_5 : xDy_2O_3$, where x is 0.2, 0.4, 0.6, 0.8 and 1.0 mol%, were prepared by the conventional melt quenching technique. For each batch about 20 g, appropriate amounts of reagent grade chemicals bismuth oxide (Bi_2O_3), boric acid (B_2CO_3), ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$) and dysprosium oxide (Dy_2O_3) powders were thoroughly mixed and ground in the porcelain crucibles. Mixing chemicals were later melted in an electrical muffle furnace for 3 hour, at 1200 °C. After complete melting, the melts were then cast into a preheated stainless steel mould before immediately transferred to an annealing furnace at 500 °C for 3 hour in order to reduce an internal mechanical stress. Finally, the as-prepared glass samples were cut and then finely polished in order to study their properties.

Measurements. The optical absorption spectra were measured by UV-Vis-NIR spectrophotometer (Shimadzu, UV-3600) in the ultraviolet, visible and near-infrared (UV-Vis-NIR) region from 200 to 2500 nm. The emission spectra and lifetime were studied by using a fluorescence spectrophotometer (Agilent Technologies, Cary Eclipse) with xenon lamp as a light source. All these measurements were recorded at room temperature.

3. Results and Discussion

The optical absorption spectra of the glass samples in the UV–VIS and NIR regions (200–2500 nm) are shown in Fig. 1. The observed eight bands (Fig. 1b) of BiBPDy glasses at 386 nm, 421 nm, 450 nm, 801 nm, 893 nm, 1094 nm, 1270 nm and 1673 nm corresponding to the absorption transitions of the Dy^{3+} ions are given in Table 1. The $^6H_{15/2} \rightarrow {}^6H_{9/2}+{}^6F_{11/2}$ transition possesses higher intensity compared to the other transitions and follows the selection rules, $|\Delta S| = 0$, $|\Delta L| \leq 2$ and $|\Delta J| \leq 2$. This transition is known as the hypersensitive transition.

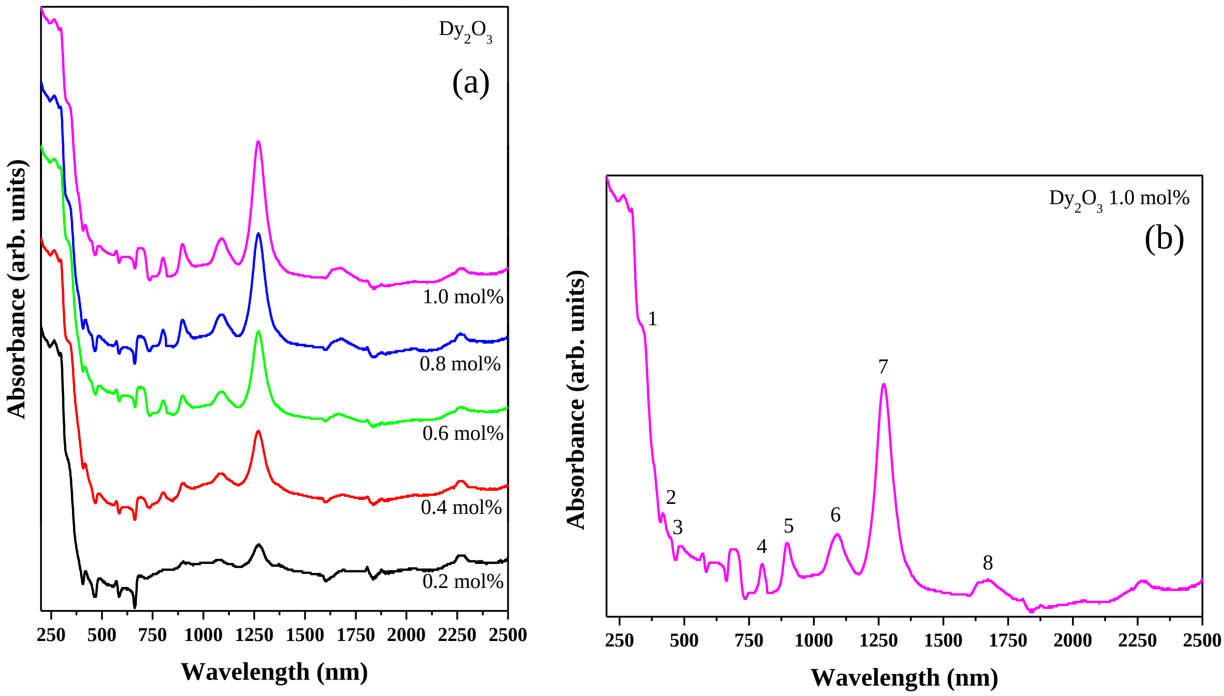

Fig. 1. The optical absorption spectra of BiBPDy glass samples for (a) all concentrations and (b) 1.00 mol% of Dy_2O_3 concentration.

Table 1. Absorption transitions of BiBPDy glass samples.

No.	Wavelength, λ (nm)	Absorption Transitions	No.	Wavelength, λ (nm)	Absorption Transitions
1	386	$^6H_{15/2} \rightarrow {}^4I_{13/2} + {}^4F_{7/2}$	5	893	$^6H_{15/2} \rightarrow {}^6F_{7/2}$
2	421	$^6H_{15/2} \rightarrow {}^4G_{11/2}$	6	1094	$^6H_{15/2} \rightarrow {}^6H_{7/2} + {}^6F_{9/2}$
3	450	$^6H_{15/2} \rightarrow {}^4I_{15/2}$	7	1270	$^6H_{15/2} \rightarrow {}^6H_{9/2} + {}^6F_{11/2}$
4	801	$^6H_{15/2} \rightarrow {}^6F_{5/2}$	8	1673	$^6H_{15/2} \rightarrow {}^6H_{11/2}$

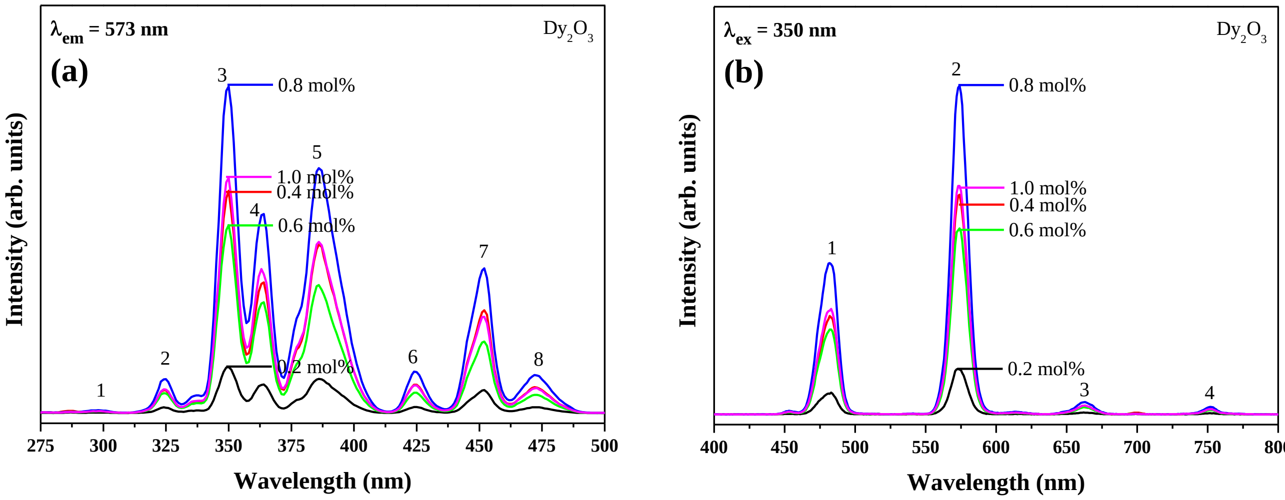

Fig. 2. Photoluminescence (a) excitation and (b) emission spectra of BiBPDy glass samples.

Table 2. Excitation transitions and emission transitions of BiBPDy glass samples.

Wavelength, λ (nm)	Excitation transitions	No.	Wavelength, λ (nm)	Emission transitions
298	$^6H_{15/2} \rightarrow {}^4K_{13/2} + {}^4H_{13/2}$	1	483	$^4F_{9/2} \rightarrow {}^6H_{15/2}$
324	$^6H_{15/2} \rightarrow {}^4K_{15/2}$	2	573	$^4F_{9/2} \rightarrow {}^6H_{13/2}$
350	$^6H_{15/2} \rightarrow {}^4M_{15/2} + {}^6P_{7/2}$	3	663	$^4F_{9/2} \rightarrow {}^6H_{11/2}$
363	$^6H_{15/2} \rightarrow {}^4I_{11/2}$	4	753	$^4F_{9/2} \rightarrow {}^6H_{9/2} + {}^4F_{11/2}$
386	$^6H_{15/2} \rightarrow {}^4I_{13/2} + {}^4F_{7/2}$	5		
423	$^6H_{15/2} \rightarrow {}^4G_{11/2}$	6		
451	$^6H_{15/2} \rightarrow {}^4I_{15/2}$	7		
473	$^6H_{15/2} \rightarrow {}^4F_{9/2}$	8		

The photoluminescence excitation (PLE) and emission (PL) spectra of the Dy^{3+} doped bismuth borophosphate glasses have been shown in Fig. 2. The PLE and PL spectra of glass samples were monitoring emissions and excitations with 573 and 350 nm wavelength, respectively. In the range of 275 – 500 nm, eight excitation bands are identified which are assigned to the electronic transitions as shown in Table 2 [14-15]. Also, four emission bands in the wavelength range 400 – 800 nm are identified and assigned in this Table. Fig. 2b reveals that as increasing Dy^{3+} concentration, the emission intensities tend to increase gradually and reaches the maximum at 0.8 mol%. However, the intensity decreased is clearly observed at the Dy^{3+} concentration beyond 0.8 mol% due to concentration quenching. In many inorganic materials, an excessive doping of emission ions usually decreases the emission intensity remarkably. The phenomenon is called concentration quenching, which is caused by the migration of excitation energy between the emission ions or energy migration to quenching centers where the excitation energy is lost by non-radiative transition.

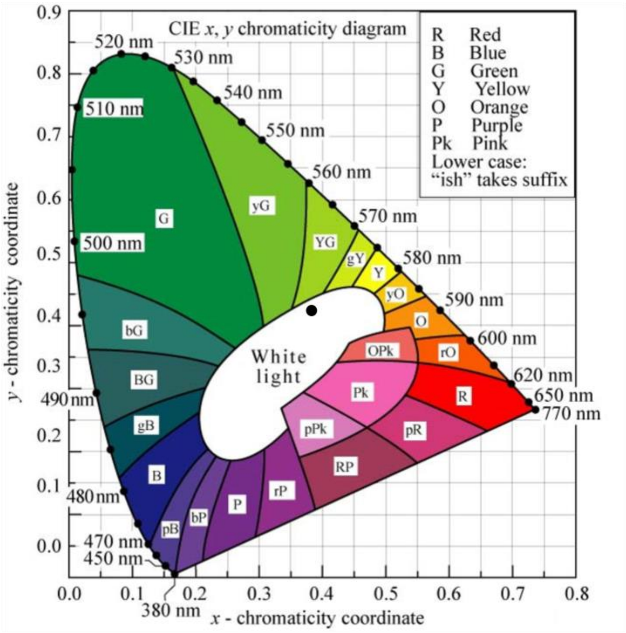

Fig. 3. CIE (*x*, *y*) chromaticity coordinates of BiBPDy glass samples.

Table 3. The CIE (*x*, *y*) chromaticity coordinates of BiBPDy glass samples under 350 nm excitation.

Dy_2O_3 concentration (mol%)	Color coordinates *x*	Color coordinates *y*
0.2	0.3831	0.4306
0.4	0.3874	0.4334
0.6	0.3854	0.4322
0.8	0.3843	0.4310
1.0	0.3846	0.4314

Most lighting specifications refer to color in terms of the 1931 CIE (Commission International de I'Eclairage) chromatic color coordinates, which recognize that the human visual system uses three primary colors: red, green and blue [16]. In general, the color of any light source can be represented as (*x*, *y*) coordinates in this color space. The CIE (*x*, *y*) chromaticity coordinates of BiBPDy glasses was calculated by the relative ration of yellow (573 nm) to blue (483 nm) emission band for glass samples under 350 nm excitation is shown in Table 3. It can be seen that the chromaticity coordinates lie with in the white light region for all conditions with increasing concentration of Dy^{3+} ions as shown in Fig. 3. This fact reveals that white light can be achieved in Dy^{3+} doped bismuth borophosphate glasses; however, the quality of the white light achieved from it may not reach the required standards of a commercial white-light-emitting diodes (WLEDs).

4. Conclusion

In summary, the Dy^{3+} ions doped bismuth borophosphate (BiBPDy) glasses were prepared by melt quenching method. All the glass samples can absorb photon in visible light and near infrared region. Emission bands of 483, 573, 663 and 753 nm for the BiBPDy glasses have been recorded. The bands with 573 nm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) and 483 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) wavelength have shown a bright fluorescent yellow and blue emission respectively, apart from 663 nm and 753 nm emission transitions. The highest intensity of emission band was obtained at 0.8 mol% Dy^{3+} ions. The CIE chromaticity coordinates for BiBPDy glasses are located in white region. Also, the BiBPDy glasses can emit white light even changed in the concentrations of Dy^{3+}. These results demonstrate that BiBPDy glass is a promising luminescence material for WLED.

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