

CHAPTER 4 RESULTS AND DISCUSSION

Although glasses can be made by a wide variety of methods, the vast majority are still produced by heat treatment and batch component at an elevated temperature. This procedure always involves the selection of raw materials, batch calculations, weighing and mixing materials to provide a homogenous and heating process, etc. A measurement and analysis glass sample is the importance process for physical and optical properties of glasses. The aim of this research was to study and characterize the properties of dysprosium doped in bismuth borate glasses.

4.1 General Characteristic of Glass Samples

This research, all chemical powder composition was reagent grade for preparation the bismuth borate glass samples with the rare-earth (Dy) doped. Batch samples for producing 30 g weight of glass samples were prepared at the melting temperature of $1,100^{\circ}\text{C}$ at 3 hours time intervals and annealed at the temperature 500°C at 3 hours time intervals to remove thermal strain. Glass samples were cooled down to room temperature. Glass samples were cut and polish to a dimension $1.0\text{ cm} \times 1.5\text{ cm} \times 0.3\text{ cm}$ for further studied and analysis, especially optical, physical, structural and luminescence properties of Dy^{3+} ions doped on the bismuth borate glass system with different Dy_2O_3 concentration. The photograph of glass samples showed as Figure 4.1. The glasses are shown yellow color in all samples.

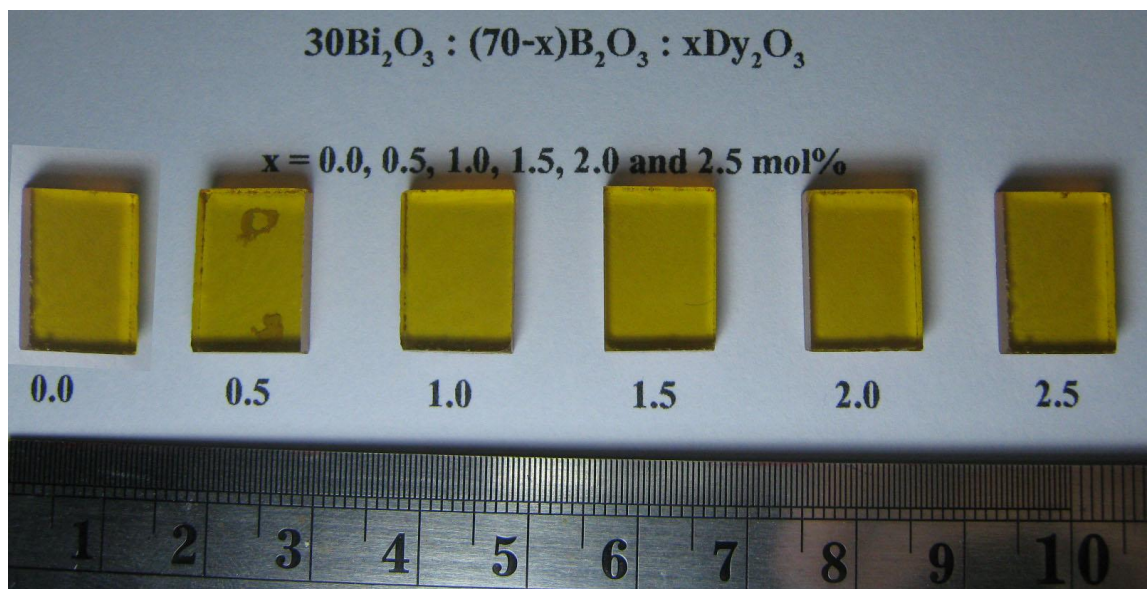


Figure 4.1 Illustration of $30\text{Bi}_2\text{O}_3 : (70-x)\text{B}_2\text{O}_3 : x\text{Dy}_2\text{O}_3$ glasses.

4.2 Amorphous Nature of Glass Samples

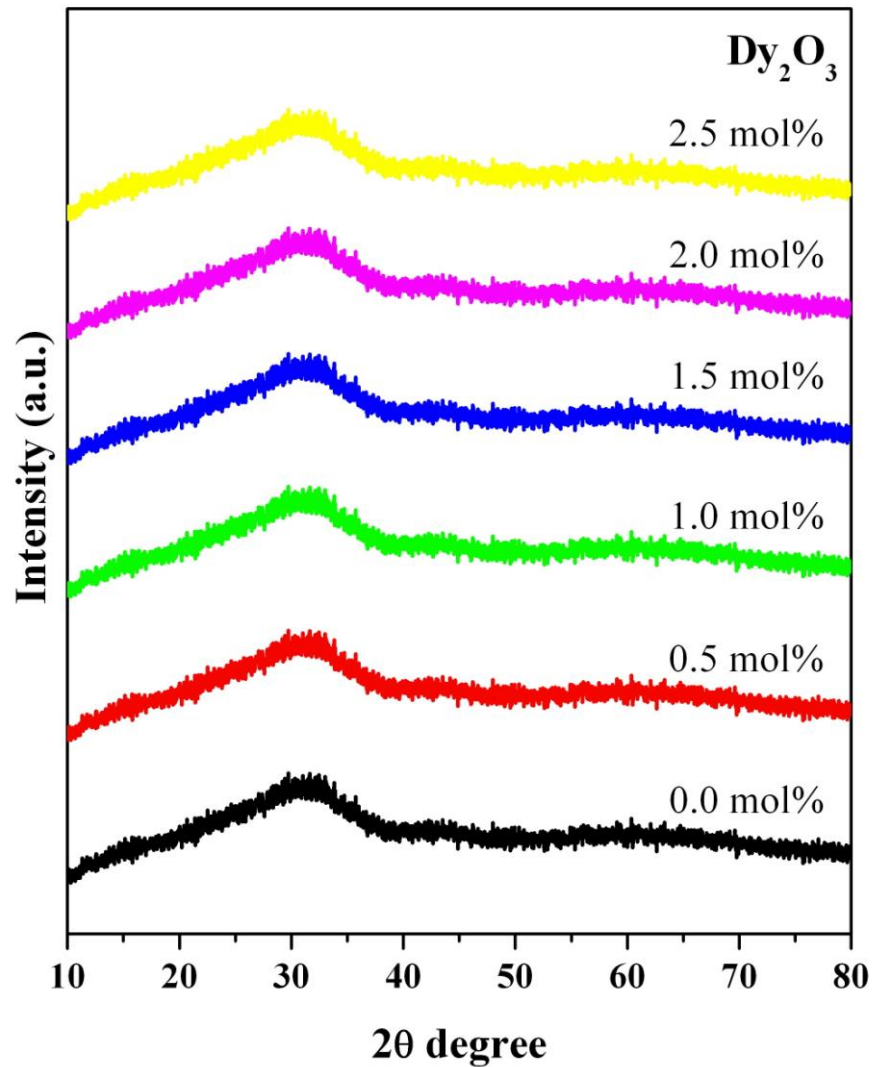


Figure 4.2 Diffraction patterns of $30\text{Bi}_2\text{O}_3 : (70-x)\text{B}_2\text{O}_3 : x\text{Dy}_2\text{O}_3$ glasses.

The amorphous nature of glasses were confirmed by x-ray diffractometer from Cu (K_α , $\lambda=1.5406 \text{ \AA}$) with an angular range $20\text{-}80$ (2θ) degree with a step length of 0.02 degree and a counting time 60 sec/step . X-ray diffraction patterns of all glass samples show a hump were observed in the 2θ about 30 degree, indicating disordered structure and amorphous nature of glass samples. The typical XRD patterns of all glasses are shown in Figure 4.2.

4.3 Density and Molar Volume

To measured density of Dy_2O_3 doped in bismuth borate glass system for different Dy_2O_3 concentrations. The variation of the density with Dy_2O_3 concentration was shown in Table 4.1 and Figure 4.3. The density is not depend on Dy_2O_3 concentration, although the relative molecular mass of Dy_2O_3 is higher than boric oxide (B_2O_3).

Table 4.1 Density, molecular weight, and molar volume of $30\text{Bi}_2\text{O}_3 : (70-x)\text{B}_2\text{O}_3 : x\text{Dy}_2\text{O}_3$ glasses.

Samples no.	Dy_2O_3 (mol%)	Density (g/cm^3)	M_T (g/mol)	V_M (cm^3/mol)
1	0.00	4.206	190.387	45.261
2	0.50	4.166	191.904	46.064
3	1.00	4.184	193.421	46.228
4	1.50	4.176	194.938	46.675
5	2.00	4.203	196.455	46.747
6	2.50	4.193	197.972	47.210

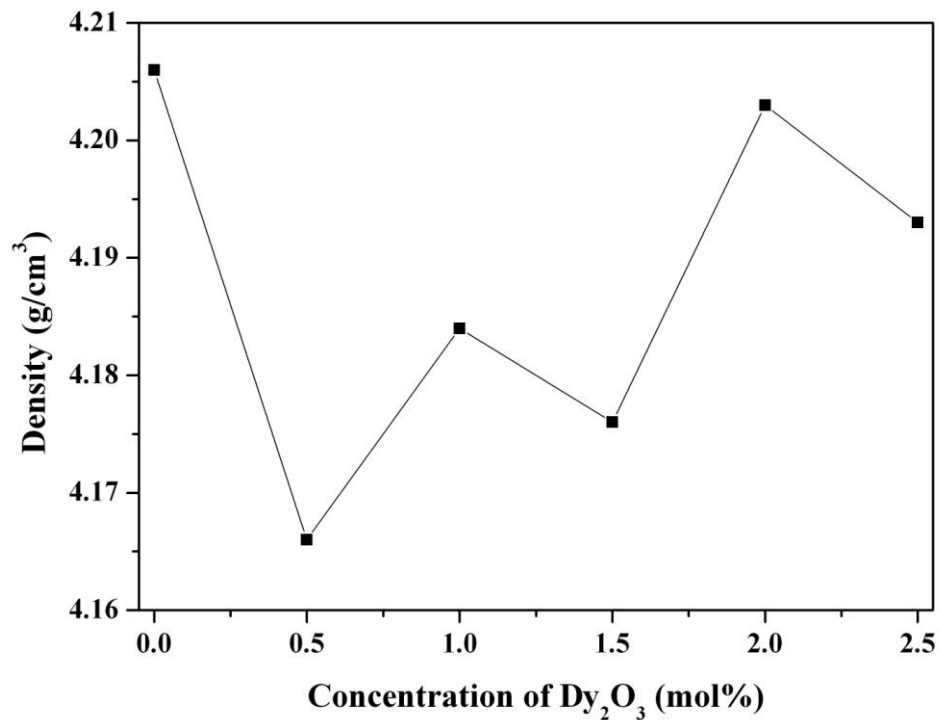


Figure 4.3 Density of $30\text{Bi}_2\text{O}_3 : (70-x)\text{B}_2\text{O}_3 : x\text{Dy}_2\text{O}_3$ glasses.

The action of modifiers in borate glasses is more complex than the one in silicate glasses. In the addition of modifier ions leads invariably to the creation of non-bridging oxygen (NBOs). In borate glasses on the other hand the modifier may act according to all three mechanisms. (a) Breaking of B-O-B bonds and creation of non-bridging oxygen, (b) Increasing the oxygen coordination of cation B, (c) A combination of both. Which one prevails depends on the modifier content. For simplicity three-coordinated boron will be denoted as B_3 and four-coordinated boron as B_4 . So, when some modifier is added, coordination number of boron atoms changes from B_3 to B_4 . As a result of this, non-bridging oxygen (NBOs) would start to form.

In this case, when add Dy_2O_3 in bismuth borate glasses. The loose packing increases due to Dy_2O_3 acts as modifier. The NBOs are increased in number in the borate network so molar volumes were increased. The increases in the molar volume is due to the increase in the bond length or inter-atomic spacing between the atoms which may be attributed to the decrease in the stretching force constants of the bonds inside the glass network. The variation of the molar volume with Dy_2O_3 concentration was shown in Table 4.1 and Figure 4.4.

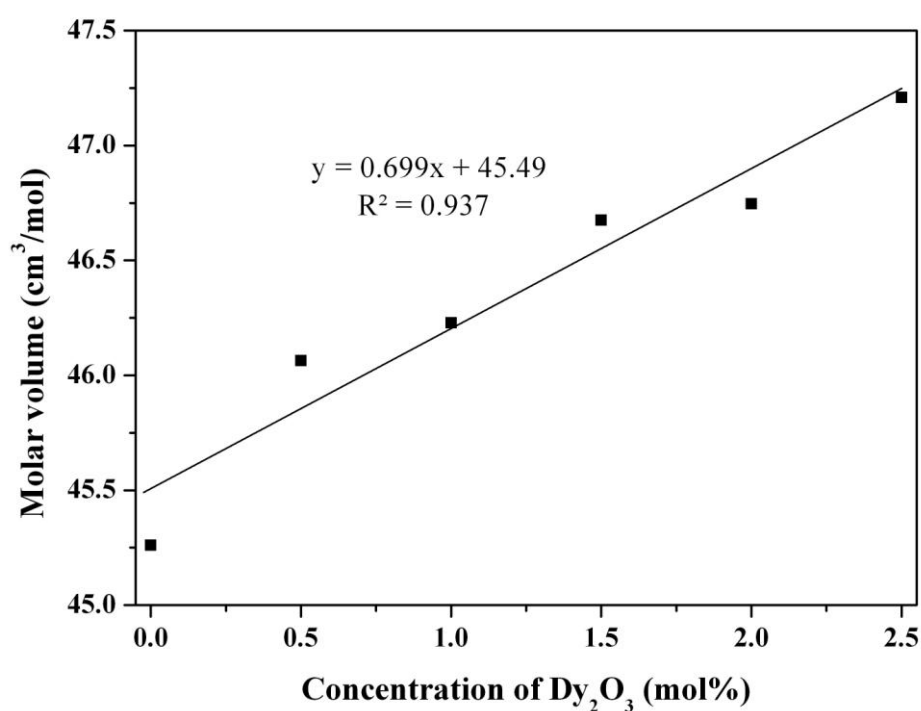


Figure 4.4 Molar volume of $30Bi_2O_3 : (70-x)B_2O_3 : xDy_2O_3$ glasses.

4.4 UV-VIS-NIR Absorption Spectra

Figure 4.5 shows the absorption spectra of bismuth borate glasses doped with Dy^{3+} at different Dy_2O_3 concentration. The bands are assigned from the ground state, $^6\text{H}_{15/2}$. The transitions from the next excited state $^6\text{H}_{13/2}$ may be ruled out due to thermalization as the energy gap between $^6\text{H}_{15/2}$ and $^6\text{H}_{13/2}$ is around $3,000\text{ cm}^{-1}$. From this spectra, the levels of $^4\text{I}_{13/2}$, $^4\text{F}_{7/2}$, $^4\text{G}_{11/2}$, $^4\text{I}_{15/2}$ are not observed. The absorption peaks at $^6\text{F}_{3/2}$ (762 nm), $^6\text{F}_{5/2}$ (805 nm), $^6\text{F}_{7/2}$ (905 nm), ($^6\text{H}_{7/2}$, $^6\text{F}_{9/2}$) (1,100 nm), ($^6\text{F}_{11/2}$, $^6\text{H}_{9/2}$) (1,280 nm), and $^6\text{H}_{11/2}$ (1,695 nm) are observed and well resolved. The position and intensity of certain transitions of rare-earth ions (Dy^{3+}) are found to be very sensitive to the environment around the ion. Such transitions are termed as hypersensitive transitions [35]. All known hypersensitive transitions obey the selection rule $|\Delta S| = 0$, $|\Delta L| \leq 2$, $|\Delta J| \leq 2$ [35]. In the case of Dy^{3+} ($4f_9$) ions, the hypersensitive transition ($^6\text{F}_{11/2}$, $^6\text{H}_{9/2}$) is found to be more intense than the other transitions.

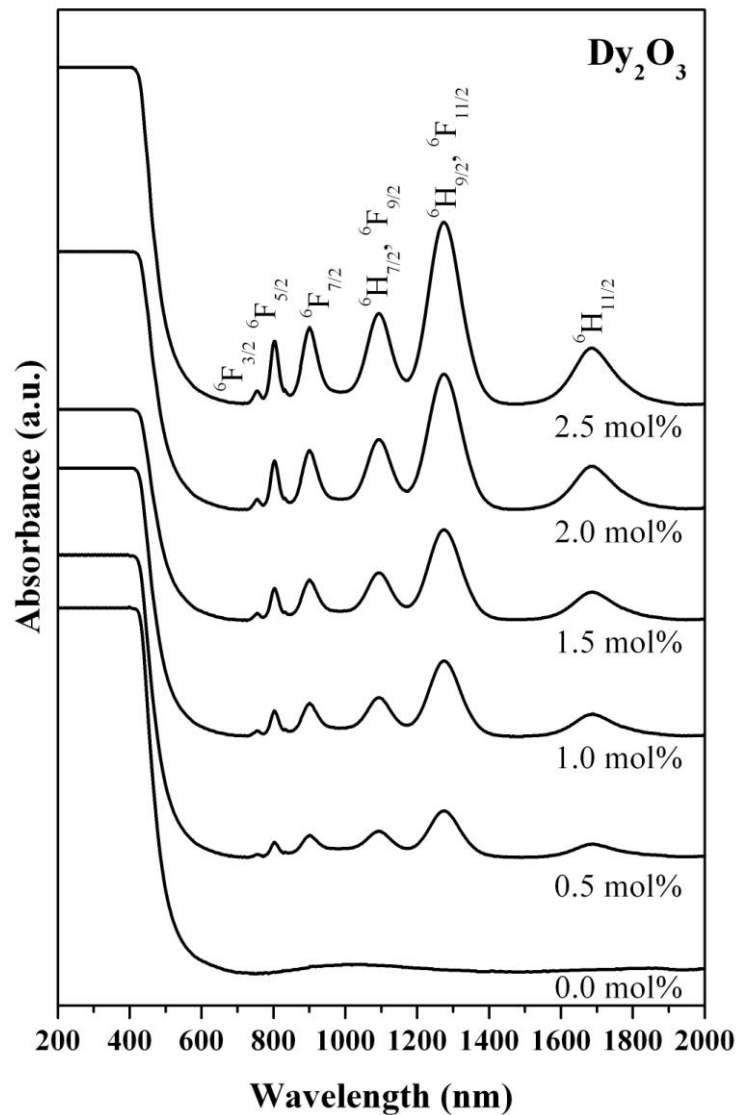


Figure 4.5 Optical absorption spectra of $30\text{Bi}_2\text{O}_3 : (70-x)\text{B}_2\text{O}_3 : x\text{Dy}_2\text{O}_3$ glasses.

4.5 Photoluminescence

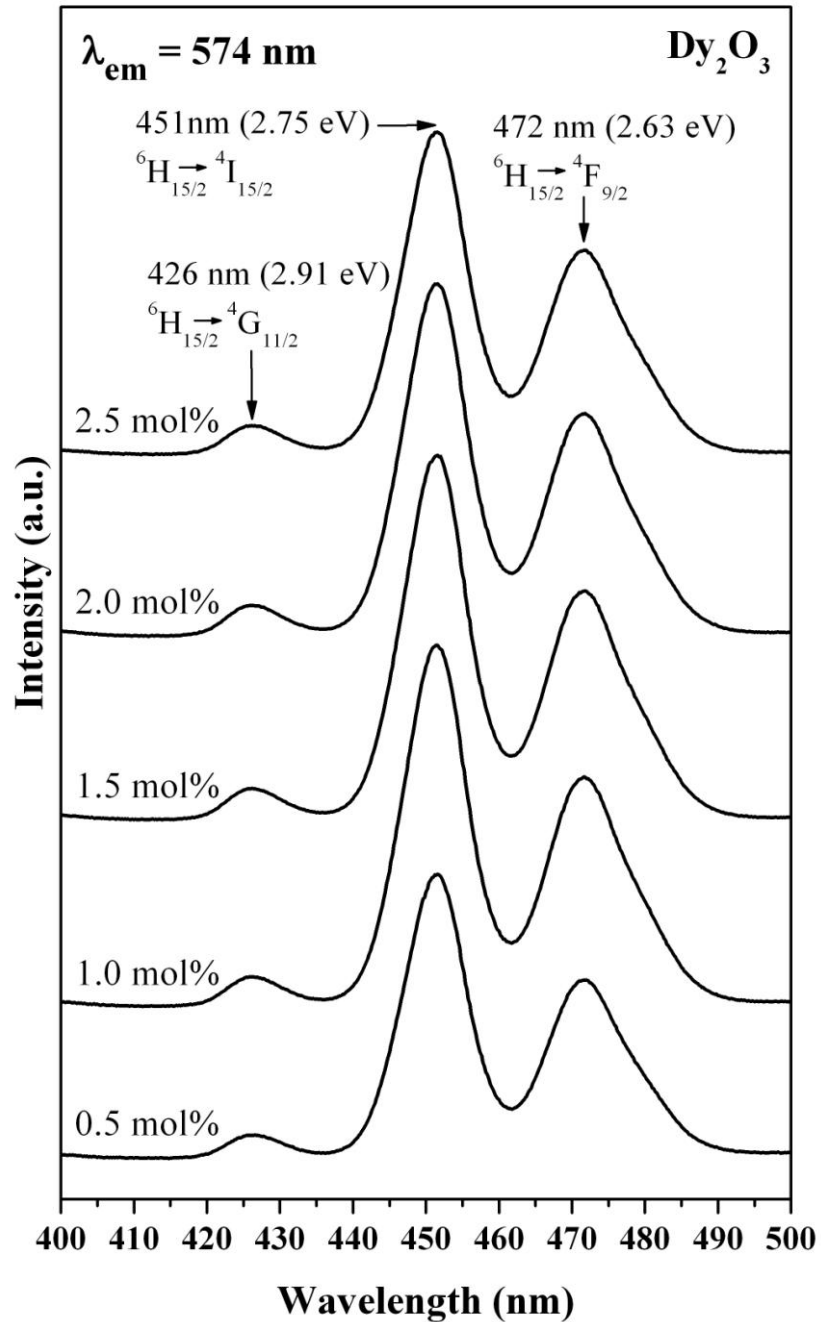


Figure 4.6 The excitation spectra of $30\text{Bi}_2\text{O}_3 : (70-x)\text{B}_2\text{O}_3 : x\text{Dy}_2\text{O}_3$ glasses.

The excitation spectra of Dy^{3+} doped in bismuth borate glasses were recorded by monitoring an intense emission at 574 nm and are shown in Figure 4.6. From the spectra, three obvious excitation peaks are observed and are assigned to the transitions originating from the ground state, ${}^6\text{H}_{15/2}$ to the excited states ${}^4\text{G}_{11/2}$ (426 nm, 2.91 eV), ${}^4\text{I}_{15/2}$ (451 nm, 2.75 eV) and ${}^4\text{F}_{9/2}$ (472 nm, 2.63 eV) of Dy^{3+} ions [36]. Two of them, ${}^6\text{H}_{15/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^6\text{H}_{15/2} \rightarrow {}^4\text{F}_{9/2}$ transitions are the most intense. Between these excitations, the prominent transition (451 nm) has been selected for the measurement of emission spectra.

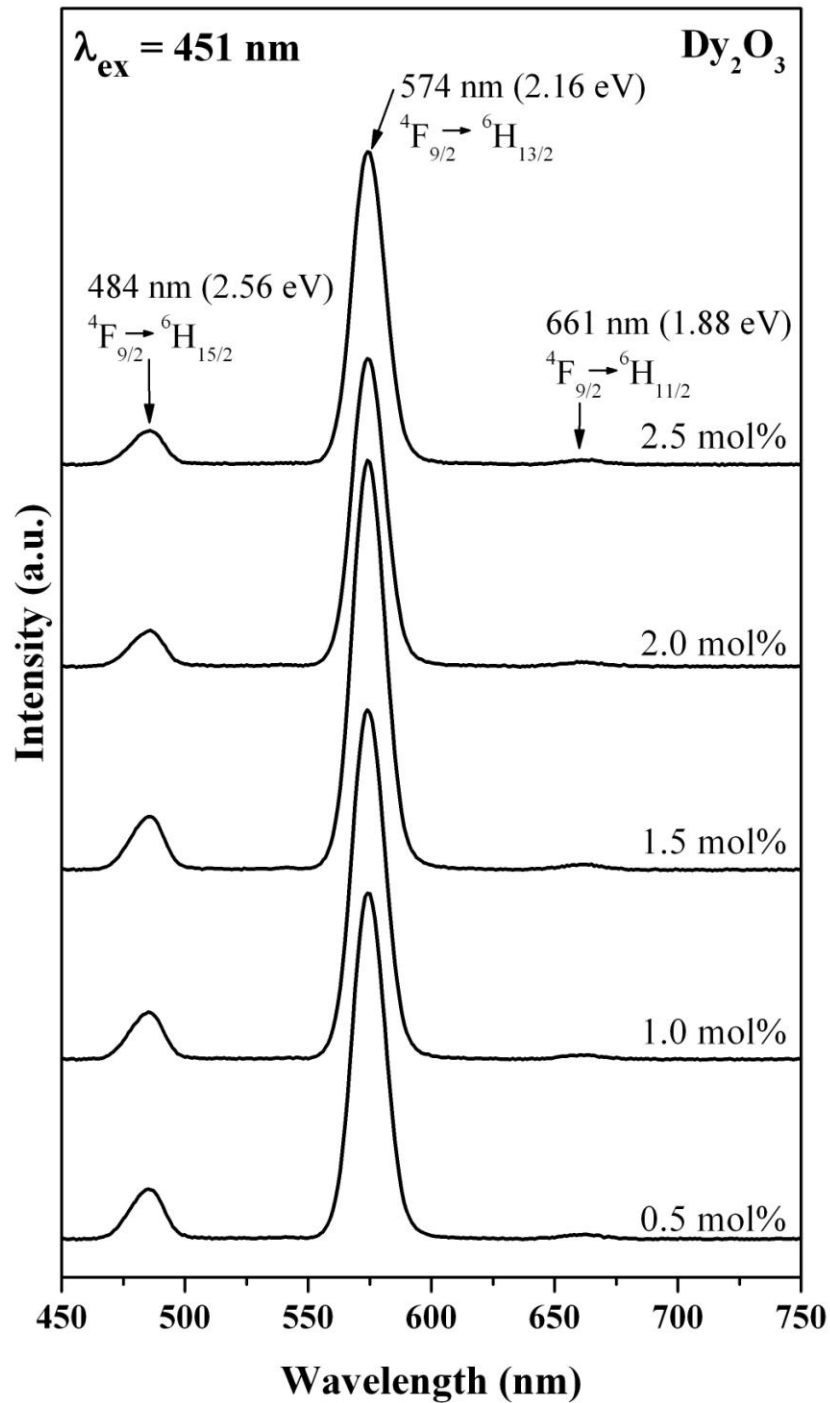


Figure 4.7 The emission spectra of $30\text{Bi}_2\text{O}_3 : (70-x)\text{B}_2\text{O}_3 : x\text{Dy}_2\text{O}_3$ glasses.

Figure 4.7 presents the emission spectra of Dy^{3+} doped in bismuth borate glasses with 451 nm (2.75 eV) excitation wavelength. When the $^4\text{I}_{15/2}$ level of Dy^{3+} is excited with 451 nm wavelength, though this level and then decays down to $^4\text{F}_{9/2}$ excited state by means of non-radiation (NR) relaxation [37]. The next eigen state of Dy^{3+} is $^4\text{F}_{9/2}$ whose energy from ground state is $21,100\text{ cm}^{-1}$. This state is separated from the next lower lying level ($^6\text{F}_{1/2}$) by about $7,000\text{ cm}^{-1}$, which makes the multiphonon relaxation negligible inspite of high phonon energies of the host (approximately 900 cm^{-1}) [38].

From this emission spectra, three emission transitions were observed, which are assigned to $^4F_{9/2} \rightarrow ^6H_{15/2}$ (484 nm, 2.56 eV), $^4F_{9/2} \rightarrow ^6H_{13/2}$ (574 nm, 2.16 eV), and $^4F_{9/2} \rightarrow ^6H_{11/2}$ (661 nm, 1.88 eV) (for blue, yellow, and red bands) transitions, respectively. All intensity of emission peaks are comparable with different Dy_2O_3 concentration. Among these three transitions, the $^4F_{9/2} \rightarrow ^6H_{15/2}$ (484 nm, blue bands) is magnetic dipole (MD) transition show weak intensity. This transition is less sensitive to the coordination environment [39]. $^4F_{9/2} \rightarrow ^6H_{11/2}$ (661 nm, red bands) show weak intensity and $^4F_{9/2} \rightarrow ^6H_{13/2}$ (574 nm, yellow bands) transition show strongest intensity related to the electric dipole (ED) transition. It was well known that the $^4F_{9/2} \rightarrow ^6H_{13/2}$ transitions of Dy^{3+} are hypersensitive electronic dipole transitions with $\Delta J = 2$, which are greatly affected by the coordination environment. The $^4F_{9/2} \rightarrow ^6H_{13/2}$ transition is a forced electric dipole transition being allowed only at low symmetries with no inversion centre [40]. When Dy^{3+} is located at low-symmetry local site (without an inversion centre), this emission is often prominent in its emission spectrum. The similar behavior was observed in the case of B_2O_3 -ZnO-PbO glasses [41] reported by G. Lakshminarayana and S. Buddhudu.

Generally, the intensity ratio of ED (yellow bands) and MD (blue bands) transitions has been used to measure the symmetry of the local environment of the trivalent 4f ions [42]. The greater the intensity of the ED transition, the more asymmetric the nature in the glass matrix [43]. In the present work, $^4F_{9/2} \rightarrow ^6H_{13/2}$ (ED) transition of Dy^{3+} ions is more intense than $^4F_{9/2} \rightarrow ^6H_{15/2}$ (MD), as a result, the studied glasses possess more asymmetry in nature. Based on the energy levels reported earlier [39,41,44] the energy level scheme for all the observed absorption, excitation and emission transitions of Dy^{3+} ion is presented in Figure 4.8.

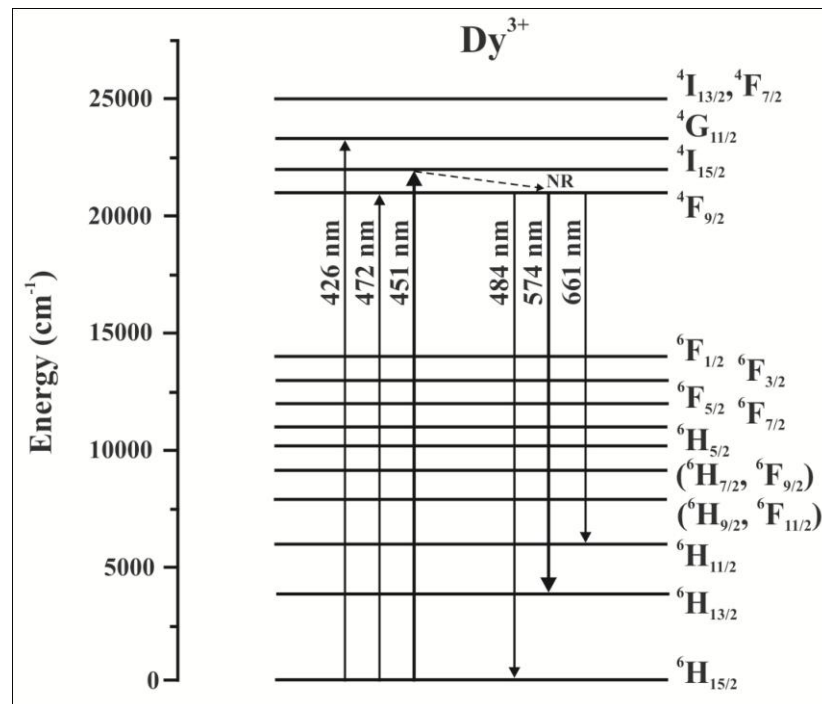


Figure 4.8 Energy level and luminescence transitions of Dy^{3+} in $30Bi_2O_3 : (70-x)B_2O_3 : xDy_2O_3$ glasses.

4.6 X-ray Luminescence

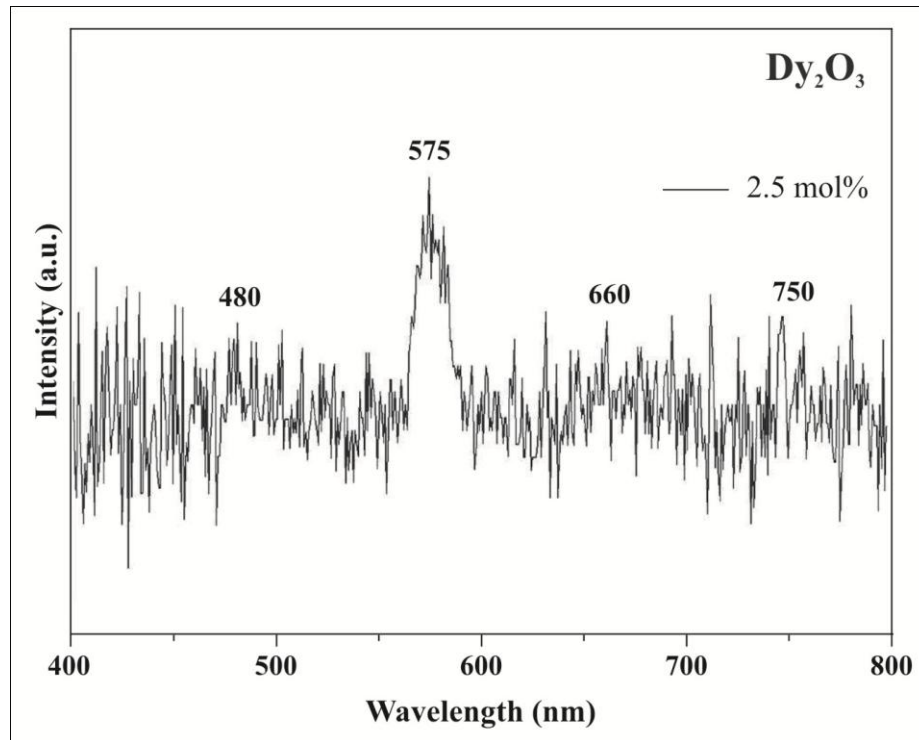


Figure 4.9 The x-ray luminescence spectra 30Bi₂O₃ : (70-x)B₂O₃ : xDy₂O₃ glasses.

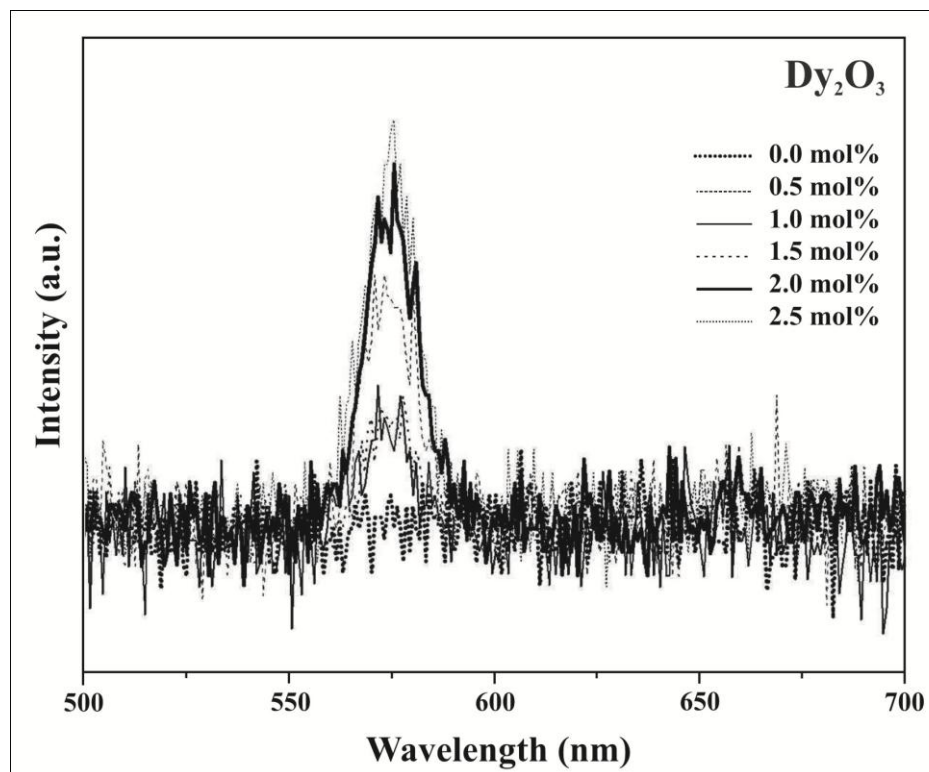


Figure 4.10 Expansion of [Figure 4.9](#), the x-ray luminescence spectra 30Bi₂O₃ : (70- x)B₂O₃ : xDy₂O₃ glasses.

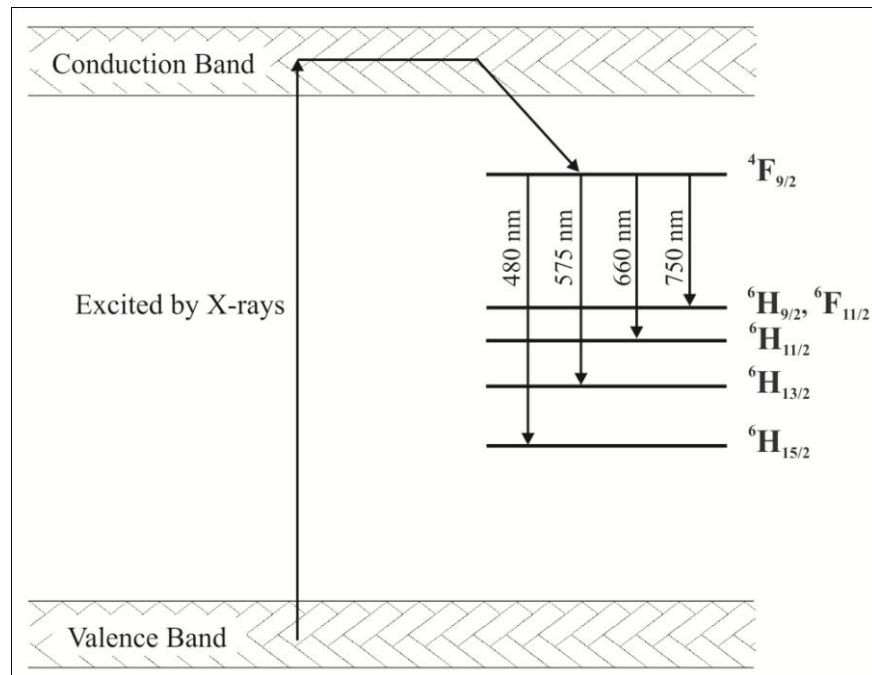


Figure 4.11 X-ray luminescence process of Dy^{3+} in $30\text{Bi}_2\text{O}_3 : (70-x)\text{B}_2\text{O}_3 : x\text{Dy}_2\text{O}_3$ glasses.

Figure 4.9 shows the x-ray luminescence spectra of different Dy_2O_3 concentration doped in bismuth borate glass at room temperature. All samples emitted a luminescence with the emission peaks at 480 nm, 575 nm, 660 nm, and 750 nm. The emission spectra peaks were due to the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ (480 nm), ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ (575 nm), ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$ (660 nm) and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{9/2} + {}^6\text{F}_{11/2}$ (750 nm) [16, 45] respectively. Figure 4.10 is expansion of Figure 4.9, it can be seen that the x-ray luminescence intensities of peak at 575 nm are slightly increased with increasing of Dy_2O_3 concentration and the strongest intensity peak at 575 nm was obtained, similar with photoluminescence results. These emission bands were showed other glass materials as $\text{P}_2\text{O}_5\text{-Al}_2\text{O}_3\text{-Na}_2\text{O:Dy}_2\text{O}_3$ [46]. The x-ray luminescence process of Dy^{3+} in $30\text{Bi}_2\text{O}_3 : (70-x)\text{B}_2\text{O}_3 : x\text{Dy}_2\text{O}_3$ glasses is shown in Figure 4.11.

4.7 Proton Luminescence

The glass sample (Dy_2O_3 2.0 mol%) was wrapped by 0.1 mm of Teflon tape for light shielding, except for one side where attached to the sample holder. The 38 MeV proton beam of 10 nA for 10 seconds irradiated 2.0 mol% Dy_2O_3 doped glass scintillator and data were taken during proton irradiation. The emission spectrum of Figure 4.12 shows that the 2.0 mol% Dy_2O_3 doped glass emits a luminescence with the emission peak at 575 nm. This result corresponds with photoluminescence and x-ray luminescence spectra.

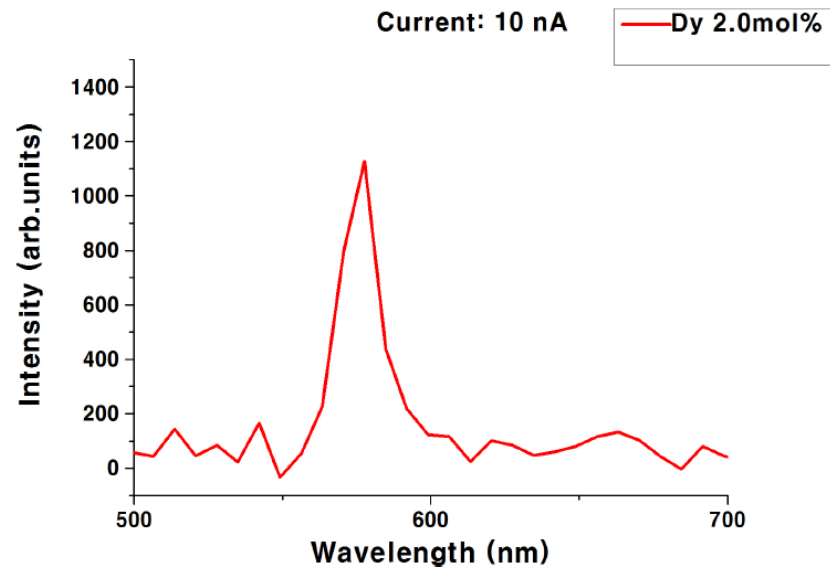


Figure 4.12 The proton luminescence spectrum $30\text{Bi}_2\text{O}_3 : (70-x)\text{B}_2\text{O}_3 : x\text{Dy}_2\text{O}_3$ glasses.