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Optical and Structural Investigation of Bismuth Borate Glasses Doped With Dy^{3+}

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Abstract

This paper reports on physical and optical properties of Dy^{3+} doped bismuth borate glasses. The glasses containing Dy^{3+} in (70-x)B_2O_3:30Bi_2O_3:xDy_2O_3 (where x = 0.0-2.5 mol%) have been prepared by melt-quenching method. In order to understand the role of Dy_2O_3 in these glasses, the density, molar volume, and optical spectra were investigated. The results show that molar volume of the glasses increase with the increasing of Dy_2O_3 concentration and consequently generating more non-bridging oxygen (NBOs) into glass matrix. The absorption spectra of Dy^{3+} doped in soda-lime silicate glass correspond with several bands, which are assigned from the ground state, $^6H_{15/2}$ to $^6F_{3/2}$(762 nm), $^6F_{5/2}$(805 nm), $^6F_{7/2}$(905 nm), ($^6H_{7/2}$, $^6F_{9/2}$) (1100 nm), ($^6F_{11/2}$, $^6H_{9/2}$)(1280 nm), and $^6H_{11/2}$(1695 nm).

Keywords: Glass, Dy^{3+}; Absorption spectra; Bismuth borate

1. Introduction

Glasses doped with rare-earth ions (RE^{n+}) are proving to be luminescence materials as they have high emission efficiencies. These emissions correspond to 4f–4f and 4f–5d electronic transitions in the RE^{n+}. The 4f–4f transition gives an especially sharp fluorescence pattern from the ultraviolet (UV) to the infrared region. This is due to shielding effects of the outer 5s and 5p orbitals on the 4f electrons. In recent years, glasses doped with rare-earth ions have drawn much attention due to their potential applications in solid-state lasers, optical amplifiers and three-dimensional displays [1]–[4].

On the other hand, for higher valent oxides, such as Bi_2O_3 when used as a modifier, the cation produces important structural effects due to its highest valence. In the literature, it is supposed that Bi_2O_3 occupy both network-forming and network modifying positions. Therefore, the physical properties of such glasses exhibit

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discontinuous changes when the structural role of the cation switches over in this way [5]. Also, glasses containing Bi_2O_3 have attracted a considerable attention because of their wide applications in the field of glass-ceramics, thermal and mechanical sensors, reflecting windows, radiation shielding and because they may be used as layers for optical and opto-electronic devices, etc. [6] These glasses have a long infrared (IR) cut-off, which makes them ideal candidates for optical transmission [7]. Bismuthate glasses containing alkali oxide act as ionic conductors and possess high conductivity compared to other heavy metal glasses [8]. However, the study of the physical properties of the ionic glasses has been paid little attention.

$Dy^{3+}(4f^9)$ doped glasses have been considered as promising laser active materials able to emit radiation associated with the $^6H_{13/2}\rightarrow{}^6H_{15/2}$ transition of Dy^{3+} ion around 3 μm [9] .The active Dy^{3+} ion provides two typical emission transitions that correspond to $^4F_{9/2}\rightarrow{}^6H_{15/2}$ (magnetic dipole) in blue (~480 nm) and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ (electric dipole) in yellow (~570 nm) regions, which are also necessary for full primary color displays [10]–[13]. In this paper we report on optical, physical and structural properties of Dy^{3+} ion-doped bismuth borate glass in formula $(70\text{-}x)B_2O_3{:}30Bi_2O_3{:}xDy_2O_3$ (where x = 0.0-2.5 mol%).

2. Materials and Method

Dy^{3+} doped bismuth borate glasses with the following composition are developed for the present work along with a reference glass.

$30.0Bi_2O_3 : 70B_2O_3$ reference glass (mol%)
$29.5Bi_2O_3 : 70B_2O_3 : 0.5Dy_2O_3$
$29.0Bi_2O_3 : 70B_2O_3 : 1.0Dy_2O_3$
$28.5Bi_2O_3 : 70B_2O_3 : 1.5Dy_2O_3$
$28.0Bi_2O_3 : 70B_2O_3 : 2.0Dy_2O_3$
$27.5Bi_2O_3 : 70B_2O_3 : 2.5Dy_2O_3$

All these glasses were prepared by using high purity grade of Bi_2O_3 (Fluka), H_3BO_3 (Fluka) and Dy_2O_3 (Fluka) as raw materials. Each batch weighing about 30 g was mixed homogeneously and melted at 1100°C for 3 h in an alumina crucible, in air. The melts were poured onto a preheat stainless steel plates. These glasses are in rectangular designs with a good transparency. All the glasses were annealed below the glass transition temperature to remove thermal strains. Finally, the as-prepared glass samples were cut and then finely polished to a dimension of 1.0cm x 2.0cm x 0.3cm for properties investigation. By applying Archimedes principle, the weight of the prepared glass samples was measured in air and in xylene using a 4-digit sensitive microbalance (AND, HR-200). Then, the density, ρ, was determined using the relation

$$\rho = \frac{W_a}{W_a - W_b} \times \rho_b \tag{1}$$

where W_a is the weight in air, W_b is the weight in xylene, and ρ_b is the density of xylene ($\rho_b = 0.863$ g/cm^3).

The corresponding molar volume (V_M) was calculated using the relation, $V_M = M_T/\rho$, where M_T is the total molecular weight of the multi-component glass system given by

$$M_T = x_{Bi_2O_3} Z_{Bi_2O_3} + x_{B_2O_3} Z_{B_2O_3} + x_{Dy_2O_3} Z_{Dy_2O_3} \tag{2}$$

Where $x_{Bi_2O_3}$, $x_{B_2O_3}$ and $x_{Dy_2O_3}$ are the mole fractions of the constituent oxides, and $Z_{Bi_2O_3}$, $Z_{B_2O_3}$ and $Z_{Dy_2O_3}$ are the molecular weights of the constituent oxides.

The optical absorption spectra were recorded at room temperature using a UV-visible-NIR spectrophotometer (Shimadzu, UV-3100), working in 190-2100 nm.

3. Results and Discussion

From table 1, although the relative molecular mass of Dy_2O_3 is higher than B_2O_3, density is found to not depend on Dy_2O_3 concentration. Boron oxide is well known conventional network former. It consists of a random three-dimensional network of 6-membered boroxol rings [14], when some modifier is added, coordination number of boron atoms changes from 3 to 4. As a result of this, non-bridging oxygens (NBOs) would start to form. It is well

reported that at low concentration of Dy_2O_3 acts as network modifier in place of network former in bismuth borate glass system. The increase in molar volume may indicate that the volume of NBO sites produced by the modifier Dy_2O_3. With the composition $30Bi_2O_3$:$70B_2O_3$, NBOs are already present and on addition of Dy_2O_3 (as modifier), concentration of NBOs increases. With the further addition of Dy_2O_3 we get the 6-membered rings with only one BO_4 tetrahedron.

Table 1 Density, molecular weight, molar volume, cutoff wavelength and optical basicity of $(70\text{-}x)B_2O_3$:$30Bi_2O_3$:xDy_2O_3 glass system.

% Dy_2O_3	Density (g/cm^3)	M_T (g/mol)	V_M (cm^3/mol)
0.0	4.206	190.387	45.261
0.5	4.166	191.904	46.064
1.0	4.184	193.421	46.228
1.5	4.176	194.938	46.675
2.0	4.203	196.455	46.747
2.5	4.193	197.972	47.210

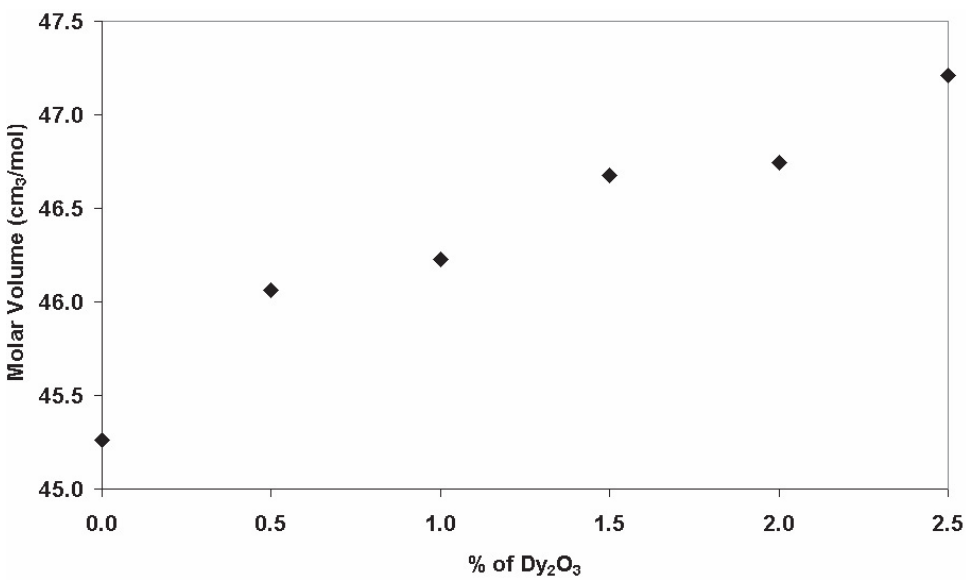

Figure 1 Molar volume of $(70\text{-}x)B_2O_3$:$30Bi_2O_3$:xDy_2O_3 glass system

The 6-membered rings with one BO_4 units can be in triborate or pentaborate forms. Due to this, NBOs further increase and the glass structure becomes more randomized. So the addition of Dy_2O_3 causes the breaking of the regular structure of the rings (borate and boroxol) and the appearance of orthoborate groups start. So the additions of network modifier do not contribute in glass formation but cleaves the structure of glass network and causes an increase in the molar volume of the glass.

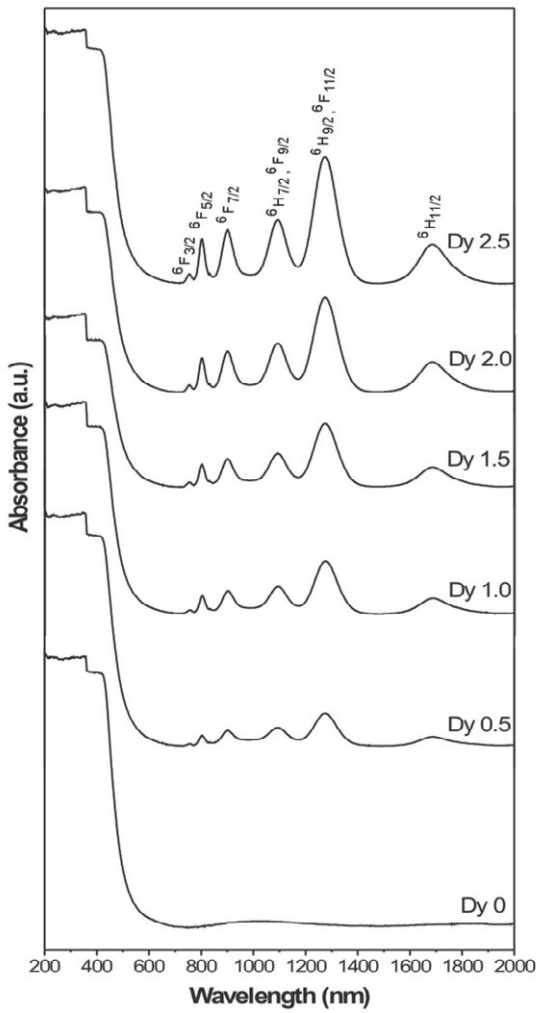

Figure 2 Optical absorption spectra of $(70\text{-}x)B_2O_3{:}30Bi_2O_3{:}xDy_2O_3$ glass system

Fig. 2 shows the absorption spectrum of bismuth borate glasses doped with Dy^{3+} at different concentration. The bands are assigned from the ground state, $^6H_{15/2}$. The transitions from the next excited state $^6H_{13/2}$ may be ruled out due to thermalization as the energy gap between $^6H_{15/2}$ and $^6H_{13/2}$ is around 3000 cm^{-1}. From this spectra, the levels of $^4I_{13/2}$, $^4F_{7/2}$, $^4G_{11/2}$, $^4I_{15/2}$ are not observed. The absorption peaks at $^6F_{3/2}$(762 nm), $^6F_{5/2}$(805 nm), $^6F_{7/2}$(905 nm), ($^6H_{7/2}$, $^6F_{9/2}$) (1100 nm), ($^6F_{11/2}$, $^6H_{9/2}$)(1280 nm), and $^6H_{11/2}$(1695 nm) are observed and well resolved. The position and intensity of certain transitions of rare-earth ions are found to be very sensitive to the environment around the ion. Such transitions are termed as hypersensitive transitions [15]. All known hypersensitive transitions obey the selection rule $|\Delta S| = 0$, $|\Delta L| \leq 2$, $|\Delta J| \leq 2$ [15]. In the case of Dy^{3+} ($^4f_9$) ion, the hypersensitive transition ($^6F_{11/2} \rightarrow {}^6H_{9/2}$) is found to be more intense than the other transitions.

4. Conclusion

Transparent bismuth borate glasses with Dy^{3+} as dopant are prepared for their optical and physical characterization. The absorption peaks at $^6F_{3/2}$(762 nm), $^6F_{5/2}$(805 nm), $^6F_{7/2}$(905 nm), ($^6H_{7/2}$, $^6F_{9/2}$) (1100 nm), ($^6F_{11/2}$, $^6H_{9/2}$) (1280 nm), and $^6H_{11/2}$(1695 nm) are observed. The molar volume were increase with Dy_2O_3 concentration, as a result of the creation of non-bridging oxygen (NBOs), which will break the bonds of the bismuth borate host glass,

and then the spaces into the network, will increase. This result indicates that the Dy_2O_3 acts as modifier in bismuth borate glass.

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