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Optical and Physical Properties of Bismuth Borate Glasses Doped With Dy^{3+}

[1]Smit Insiripong, [2]Parnuwat Chimalawong, [3,4]Jakrapong Kaewkhao and [1,4]Pichet Limsuwan
[1]Department of Physics, Faculty of Science, King Mongkut's
University of Technology Thonburi, 10140, Bangkok
[2]Physics Program, Faculty of Science, Chandrakasem Rajabhat University, 10900, Bangkok
[3]Center of Excellence in Glass Technology and Materials Science,
Nakhon Pathom Rajabhat University, 73000, Nakhon Pathom
[4]Thailand Center of Excellence in Physics, CHE, Ministry of Education,
Bangkok 10400, Thailand

Abstract: This study reports on physical and optical properties of Dy^{3+} doped bismuth borate glass. The glasses containing Dy^{3+} in $(70\text{-}x)B_2O_3{:}30Bi_2O_3{:}xDy_2O_3$ (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 bismuth borate glass correspond with several bands, which are assigned from the ground state, $^6H_{15/2}$ to $^6F_{3/2}$(761 nm), $^6F_{5/2}$(806 nm), $^6F_{7/2}$(907 nm), ($^6H_{7/2}$, $^6F_{9/2}$)(1099 nm), ($^6F_{11/2}$, $^6H_{9/2}$) (1283 nm) and $^6H_{11/2}$(1695 nm). Moreover, the optical basicities were also theoretically determined.

Key words: Absorption spectra, optical basicity, Ultra Violet (UV), Rare-Earth ions (RE^{n+}), glass transition temperature, thermalization, bismuth, borate glass, luminescence, valent oxides, radiation, long infrared

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 Ultra Violet (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 (Malchukova *et al*., 2005; Vetrone *et al*., 2002; Biju *et al*., 2004; Lakshminarayana *et al*., 2009).

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 discontinuous changes when the structural role of the cation switches over in this way (Baia *et al*., 2003). 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 (Venkataraman and Varma, 2006). These glasses have a Long Infrared (IR) cut-off, which makes them ideal candidates for optical transmission (Bale *et al*., 2008). Bismuthate glasses containing alkali oxide act as ionic conductors and possess high conductivity compared to other heavy metal glasses (Gahlot *et al*., 2005). 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 (Praveen a *et al*.,2008) .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

Corresponding Author: S. Insiripong, Department of Physics, Faculty of Science, King Mongkut's, University of Technology Thonburi, Bangkok 10140 Thailand

(~570 nm) regions, which are also necessary for full primary color displays **(**Barkyoumb *et al*., 1997; Tanabe *et al*., 1998; Yu *et al*., 2002; Lakshminarayana *et al*., 2008**)**.

In this study we report on optical, physical and structural properties of Dy^{3+} ion-doped bismuth borate glass in formula (70-x)B_2O_3:30Bi_2O_3:xDy_2O_3 (where x = 0.0-2.5 mol%).

MATERIALS AND METHODS

Glass preparation: Dy^{3+} doped bismuth borate glasses with the following compositions (in mol%) are developed for the present work along with a reference glass:

D0BB: 30.0Bi_2O_3 : 70B_2O_3 (reference glass)
D05BB: 29.5Bi_2O_3 : 70B_2O_3 : 0.5Dy_2O_3
D10BB: 29.0Bi_2O_3 : 70B_2O_3 : 1.0Dy_2O_3
D15BB: 28.5Bi_2O_3 : 70B_2O_3 : 1.5Dy_2O_3
D20BB: 28.0Bi_2O_3 : 70B_2O_3 : 2.0Dy_2O_3
D25BB: 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 1.0×2.0×0.3cm for properties investigation.

Measurements: By applying Archimedes principle, the weight of the prepared glass samples was measured in air and in xylene using a 4-digit sensitive microbalance (Denver, Pb214). Then, the density, ρ, was determined using the relation:

$$\rho = \frac{W_a}{W_a - W_b} \times \rho_b \quad (1)$$

Where:
W_a = The weight in air, W_b is the weight in xylene
ρ_b = The density of xylene (ρ_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:

$$M_T = x_{Bi_2O_3} Z_{Bi_2O_3} + x_{B_2O_3} Z_{B_2O_3} + x_{Dy_2O_3} Z_{Dy_2O_3} \quad (2)$$

Where:

$x_{Bi_2O_3}$, $x_{B_2O_3}$ and $x_{Dy_2O_3}$ = The mole fractions of the constituent oxides
$Z_{Bi_2O_3}$, $Z_{B_2O_3}$ and $Z_{Dy_2O_3}$ = 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.

RESULTS

Based on the determined density, the various physical properties of the glass studied are present in Table 1. Therefore, the Figs. 1-2 illustrate density and molar volume, respectively, as function of Dy_2O_3 concentration (%mol). Figure 3 shows the typical absorption spectrum of bismuth borate glasses undoped and doped with Dy^{3+} 0.5-2.5 % mol.

Table 1: Density, molecular weight, molar volume and optical asicity of (70-x)B_2O_3:30Bi_2O_3:xDy_2O_3 glass system

Percent Dy_2O_3	Density (g cm^{-3})	M_T (g mol^{-1})	V_M (cm^3 mol^{-1})	Optical basicity
0.000	4.206	190.387	45.261	0.6545
0.500	4.166	191.904	46.064	0.6571
1.000	4.184	193.421	46.228	0.6597
1.500	4.176	194.938	46.675	0.6623
2.000	4.203	196.455	46.747	0.6649
2.500	4.193	197.972	47.210	0.6675

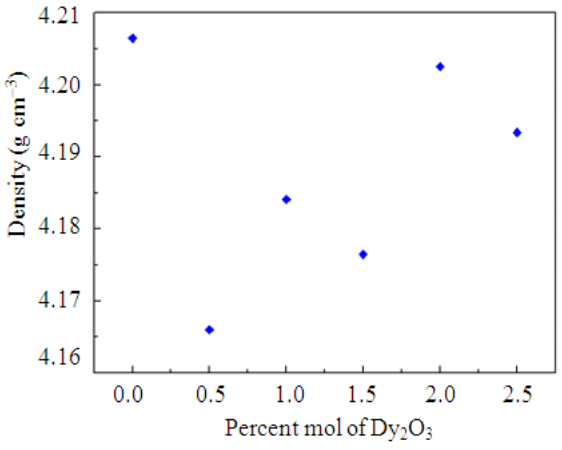

Fig. 1: Density of (70-x)B_2O_3:30Bi_2O_3:xDy_2O_3 glass system

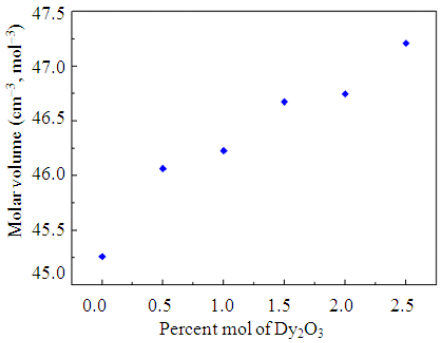

Fig. 2: Molar volume of (70-x)B_2O_3:30Bi_2O_3:xDy_2O_3 glass system

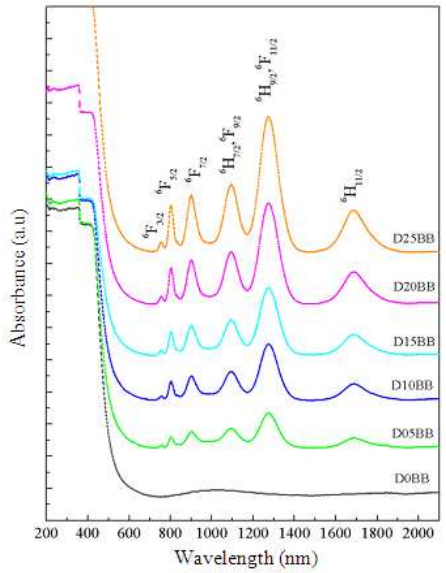

Fig. 3: Optical absorption spectra of (70-x)B_2O_3:30Bi_2O_3:xDy_2O_3 glass system

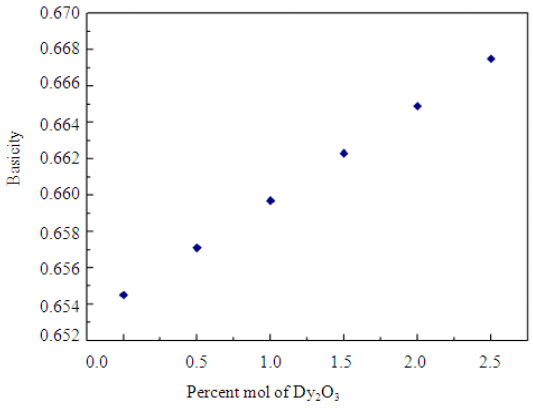

Fig. 4: Basicities of (70-x)B_2O_3:30Bi_2O_3:xDy_2O_3 glass system

In multi-component oxide glasses, the theoretical basicity, Λ_{th}, was calculated based on the basis of the equation given by:

$$\Lambda_{th} = x_1\Lambda_2 + x_2\Lambda_2 + x_3\Lambda_3 + ... \quad (3)$$

Where:

Λ_1, Λ_2 and Λ_3 = Basicities of the oxide components
x_1, x_2 and x_3 = Their equivalent fractions (fraction of the total oxygen provided by the component oxide glass)

The optical basicity of the glass samples are evaluated and listed out in Table 1. Figure 4 illustrate optical basicity as a function of Dy_2O_3 concentration (%mol).

DISCUSSION

Physical properties: From Fig. 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 (Suzuki *et al*., 2002), 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. So, the increase in molar volume (Fig. 2) may indicate that the volume of NBO sites produced by the modifier Dy_2O_3.

Optical absorption: The optical absorption edges are not sharply defined in glass samples under study, in accordance with their amorphous nature (Chimalawong *et al*., 2010). It is observed that the absorption intensity of the observed bands increase with the increase of Dy_2O_3 concentration. From the Fig. 3, the spectra consist of various absorption levels corresponding to the transitions between the ground state and higher energy states. 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 (Jorgensen and Judd, 1964). All known hypersensitive transitions obey the selection rule $|\Delta S| = 0$, $|\Delta L| \leq 2$, $|\Delta J| \leq 2$ (Jorgensen and Judd, 1964). 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.

Optical basicity: Theoretical optical basicity serves in the first approximation as a measure of the ability of oxygen to donate a negative charge in the glasses. The theoretical optical basicity can be used to classify the covalent/ionic ratios of the glasses since an increasing Λ_{th} indicates decreasing covalency (Sindhu *et al*., 2007). In context of modification, therefore, we may note the following: modifier oxides should be more basic than the glass forming oxides. When modifier oxides are added to glass-forming oxides, the resulting modification reaction is like and acid-base reaction in which the sites in the acidic (glass forming) oxide are approached by the oxide ion (of the modifier) in the order of decreasing acidities. It is clearly observed from Fig. 4 that the optical basicity increases when B_2O_3 is replaced by one of the trivalent metal dysprosium oxide. The increase of optical basicity in this work means the higher ability of oxide ions to transfer electrons to the surrounding cations.

CONCLUSION

The Dy^{3+}-doped bismuth borate glasses were prepared at various doping concentration of Dy_2O_3 and characterized for their physical and optical properties. The density and molar volume increase with increasing concentration of Dy_2O_3. The increase of molar volume with Dy_2O_3 content indicates that the extension of glass network due to the increase in the number of NBOs. The optical spectra were characterized using UV-VIS-NIR spectroscopy and show the six absorption bands in the range 190-2100 nm. The rise of optical basicity in the present glasses indicates the higher ability of oxide ions to transfer electrons to the surrounding cations.

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