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Physical, optical and luminescence properties of sodium barium bismuth borate glasses doped with dysprosium ions

Nattapon Srisittipokakun[1,2], Pornnapha Mangthong[1,2*] and Jakrapong Kaewkhao[1,2]

[1]Center of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand

[2]Physics Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, 73000, Thailand

Abstract

Sodium barium bismuth borate glass samples (NaBaBiB) doped with various concentrations of Dy^{3+} ions were produced using the conventional melt quenching technique at 1,100 °C for 3 hours. The physical, optical and luminescence properties of the NaBaBiB glasses that were produced investigated. The results showed that the density and refractive index of the glass samples increased with increasing Dy_2O_3 concentration. The optical absorption spectra of glasses were measured in the wavelength of 200 – 1,800 nm. The intensity of all of the absorption bands increased with increasing concentrations of Dy_2O_3 in the sample. The luminescence properties of Dy^{3+} doped NaBaBiB glasses were investigated. The emission spectra for glasses showed peaks at 483, 576 nm and 665 nm. These corresponds to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^6H_1 3/2$ and $^6H_{11/2}$ transitions under 453 nm excitation. The optimal concentration of Dy_2O_3 in NaBaBiB glasses was found to be 1.5 mol%.

Keywords: dysprosium oxide, physical properties, optical properties, luminescence properties, glasses

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1. Introduction

The developmental sustainability society depends on the overcoming of the current environmental pollution and energy crises. To overcome these problems, new sources of technology and energy saving devices are needed. Light emitting diodes, LEDs, are examples of such environmentally friendly and energy saving devices. Different rare earth ions activated with inorganic phosphor materials have gained the attention of many researchers owing to their potential. They also have a broad range of applications in the field of luminescent devices. These applications include; solid state lasers, optical filters, cathode ray tubes, fluorescent lamps, plasma displays, field emission displays and white light emitting diodes [1, 2]. Glass is considered, by many, to be fascinating material. This is because it can be created with a wide range of compositions each giving it different properties [3]. Through the addition of rare earth ions to the glass matrix, glass can be produced which is a promising candidate for use in solid state light applications. It has been discovered that the compositions and preparation conditions of the glass strongly affects its structural, physical and optical properties [4]. Borate oxide glass has several commercial applications. This is because of its high thermal expansion coef?cient, low melting point and softening temperature, high electrical conductivity and its optical characteristics. Borate glass which contains Barium oxide exhibits good solubility of rare earth ions and gives good optical properties. The addition of sodium oxide reduces the melting temperature of the glass. Bismuth oxide cannot be considered as a glass network former on its own due to the low field strength of its Bi^{3+} ions. However, in combination with B_2O_3 it is possible to obtain glass in a large range of different compositions.

Dysprosium (Dy^{3+}) is considered to be a superior white light emission ion compared to other rare earth ions [5]. In this work, a series of six glass samples with composition of (30-x)B_2O_3: 30Na_2O: 10Bi_2O_3: 30BaO: xDy_2O_3, with x = 0.0, 0.1, 0.5, 1.0, 1.5 and 2.0 mol% were prepared. Their physical properties were analyzed and are reported as a function of the Dy^{3+} concentration in each sample.

*Corresponding author; email: Pmangthong@hotmail.com

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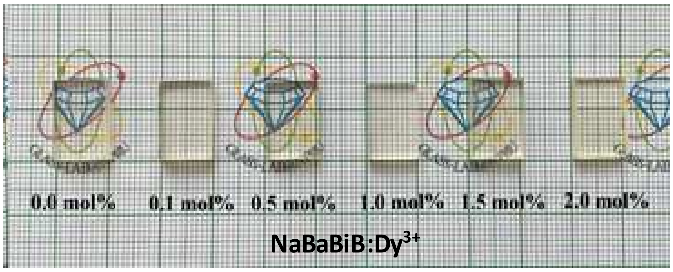

Figure 1: Photograph of the NaBaBiB:Dy^{3+} glass samples.

2. Objectives

Glass samples with chemical compositions (30-x) B_2O_3: $30Na_2O$: $10Bi_2O_3$: 30BaO: xDy_2O_3 (were labelled as NaBaBiB: Dy^{3+}) with x = 0.0, 0.1, 0.5, 1.0, 1.5 and 2.0 mol% were produced using the melt quenching technique. Required quantities of B_2O_3, Na_2O, Bi_2O_3, BaO, and Dy_2O_3 were weighed separately in an electronic balance before being mixed thoroughly. The mixtures were melted in an alumina crucible at 1,200 °C for 3 hours in an electric furnace. The homogenized melt was poured onto a graphite mound. The mound was preheated to avoid the breaking samples due to thermal stress. The sample was then pressed with another plate to obtain a square-shape. In order to prevent breaks and cracks, these glass samples were immediately annealed at 500 °C for 3 hrs and then cooled slowly to room temperature. Finally, glass samples were cut and finely polished to the dimensions of 1.0 cm × 1.5 cm × 0.3 cm.

The densities of glass samples were measured using the Archimedes' principle:

$$\rho_{\text{sample}} = \left(\frac{W_A}{W_A - W_B}\right) \times \rho_{\text{fluid}} \quad (g/cm^3) \qquad (1)$$

Where W_A, W_B are the weight of the sample in air and in water, respectively and ρ_{sample}, ρ_{fluid} are the density of the glass samples and liquid, respectively.

$$V_M = \frac{M}{\rho} \quad (cm^3/mol) \qquad (2)$$

When M is average molecular weight and ρ is the density of the glass sample.

The refractive index were measured by using an Abbe refractometer (ATAGO) with a sodium vapour lamp as the light source. This emitted light at a wavelength, λ of 589.3 nm (D line) and had monobromonaphthalene as a contact layer between the sample and prism of the refractometer [6, 7].

The optical absorption spectra of the samples were recorded in the UV to NIR regions in the wave length range of 200–1800 nm using a UV-VIS-NIR spectrophotometer (UV-3600, Shimadzu). Luminescence spectra measurements were carried out using a fluorescence spectrophotometer (Cary Eclipse) with a xenon flash lamp. All of the measurements that were carried out were performed at room temperature.

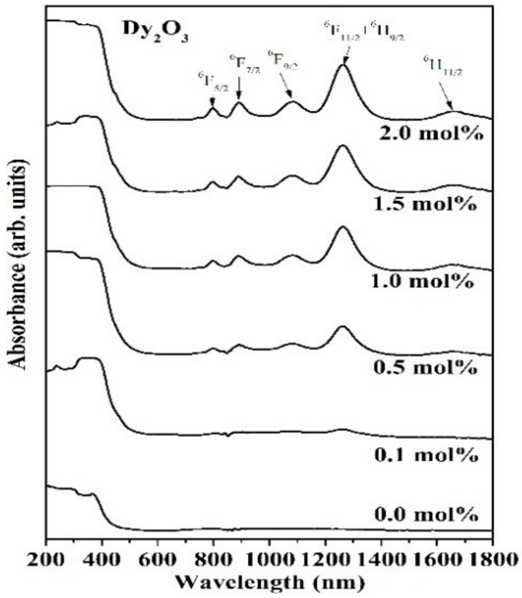

Figure 2: The absorption spectra of NaBaBiB:Dy^{3+} glasses.

3. Results and Discussion

The polished NaBaBiB:Dy^{3+} glass samples with are shown in Fig. 1. It was found that all of the glass samples produced were transparent and colorless for the full range of Dy^{3+} ion concentrations that were studied.

3.1. Physical properties

The density, molar volume and refractive index of NaBaBiB:Dy^{3+} glass samples are shown in Table 1. It was observed that the density and refractive index increased along with increasing Dy^{3+} concentration. This was thought to be due to the fact that the molecular weight of Dy_2O_3 is larger than B_2O_3. This leads to an increase in the molecular mass and density of the samples. As the density of the glass samples was increased the structure of the glass became more compact. This in turn slowed the velocity of light in the glass which in turn caused the refractive index to increase. As the Dy^{3+} ion content was increased it was found that the molar volume of the samples decreased

Table 1. Physical properties of NaBaBiB:Dy^{3+} glasses.

Concentration of Dy_2O_3 (mol%)	Density (g/cm^3)	Refractive index	Molar volume(cm^3/mol)
0.0	3.5950 ± 0.0001	1.6410	35.9423
0.1	3.6301 ± 0.0003	1.6418	35.6810
0.5	3.6848 ± 0.0003	1.6431	35.4914
1.0	3.7644 ± 0.0004	1.6466	35.1563
1.5	3.8499 ± 0.0007	1.6492	34.7817
2.0	3.9246 ± 0.0010	1.6515	34.5190

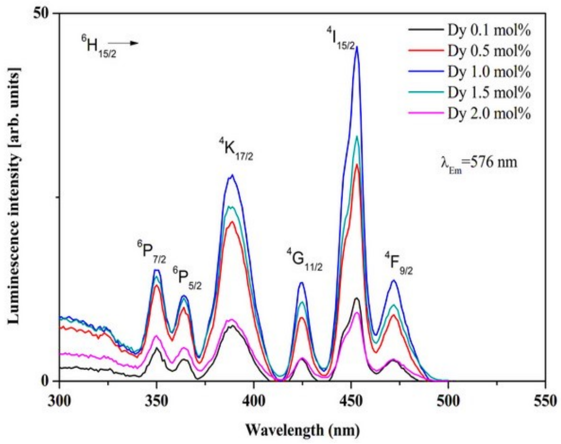

Figure 3: The excitation spectra of NaBaBiB:Dy^{3+} glasses.

and the density of the samples increased. This is not suprising as the definition of density is the mass of the glass sample divide by the molar volume of the glass sample. In addition to this it is possible that the Dy^{3+} ion substitution inside the glass network could make the glass matrix become more Dense. This in turn decreases the intermolecular spacing leading to an additional increase in density [8, 9].

3.2. Absorption spectra analysis

Absorption spectra bands can be assigned to electronic transitions of Dy^{3+} ions which originate from the ground state $^6H_{15/2}$ to various excited states (as seen in Fig. 2 [10]) such as $^6F_{5/2}$ (793 nm), $^6F_{7/2}$ (886 nm), $^6F_{9/2}$ (1078 nm), $^6F_{11/2}$+$^6H_{9/2}$ (1264 nm) and $^6H_{11/2}$ (1656 nm), respectively. It was found that the absorption intensity of all bands increased with increasing Dy2O3 concentrations. Among these transitions, the $^6F_{11/2}$+$^6H_{9/2}$ (1264 nm) was found to exhibit the strongest intensity.

3.3. Luminescence properties

In order to investigate the luminescence properties of the glass samples, it is important to know the excitation wavelength of the Dy^{3+} ions. In order to do this the excitation spectra of NaBaBiB:Dy^{3+} glass samples were recorded by monitoring emission bands at 576 nm. Fig. 3 shows the six bands that were observed in the excitation spectra at 350, 363, 388, 424, 453 and 471 nm. These correspond to transitions from the ground state to excited states of $^6H_{15/2}$ to $^6P_{7/2}$, $^6P_{5/2}$, $^4K_{17/2}$, $^4G_{11/2}$, $^4I_{15/2}$ and $^4F_{9/2}$ respectively. When compared with the other transitions, the transition $^6H_{15/2} \rightarrow {}^4I_{15/2}$ is considerably more intense. It was therefore used as an excitation wavelength to monitor the emission spectra of the glass samples.

Photons with a wavelength of 453 nm can be mostly absorbed in the visible light region. For this reason this wavelength was used to excite the glass samples in order to observe their emission spectra. The results of this are shown in Fig. 4(a). The emissions that were recorded consist of three characteristic bands of Dy^{3+} ion excitation. These were centered at 483 (blue), 576 (yellow) and 665 nm (red). These represented Dy^{3+} energy transition from $^4F_{9/2}$ excited state to lower states such as $^6H_{15/2}$, $^6H_{13/2}$ and $^6H_{11/2}$, respectively.

From Fig. 4(b), it is clear to see that the peak intensities of $^4F_{9/2}$ to $^6H_{15/2}$, $^6H_{13/2}$ and $^6H_{11/2}$ transitions were found to increase with the increasing Dy^{3+} concentration up to 1.5 mol%. It is reduced dramatically after this concentration. Fig. 5 shows the energy level diagram for the NaBaBiB:Dy^{3+} glass samples. It can be seen that the excitation energies are greater than the energy at the $^4F_{9/2}$ level. It is thought that the excess energy is lost through non-radiative channels. This thereby enhances the population of the $^4F_{9/2}$ level where the radiative emission takes place. Various radiative and non-radiative transitions are also shown in Fig. 5 [11, 12].

4. Conclusions

NaBaBiB:Dy^{3+} glass samples were produced using the conventional melt quenching technique with different Dy_2O_3 concentrations. Their physical properties were investigated through the measurement of their densities, absorption spectra, excitation characteristics and emission spectra. The density and the refractive indexes were found to increase with increasing concentrations of Dy_2O_3 while the molar volume was found to decrease. The absorption spectra of samples was recorded in the wavelength range 200–1800 nm. The glass samples showed strong absorption bands in the NIR region at 1264 nm. The PL luminescence spectra for the samples showed two major peaks at 483, 576 nm and a minor peak at 665 nm. These

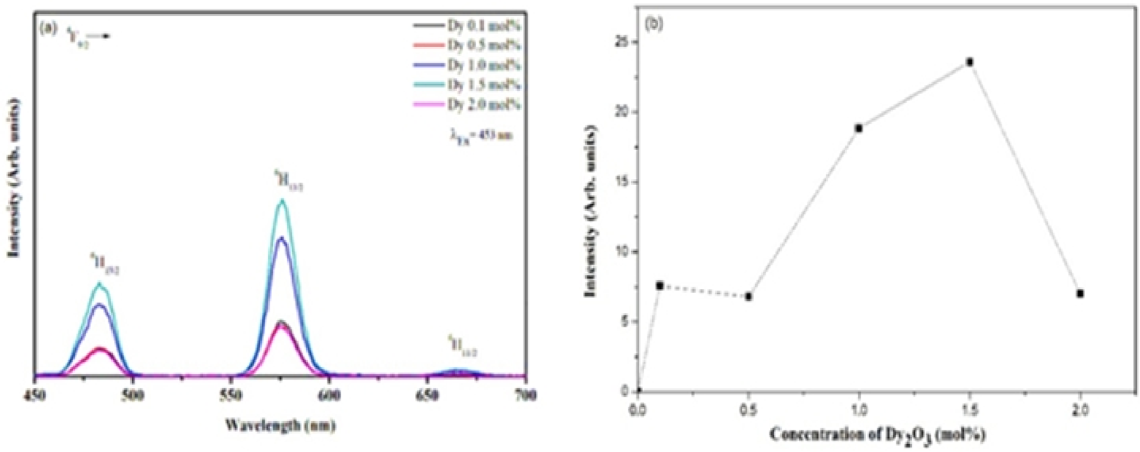

Figure 4: The emission spectra of NaBaBiB:Dy^{3+} glasses with different Dy^{3+} ions concentration.

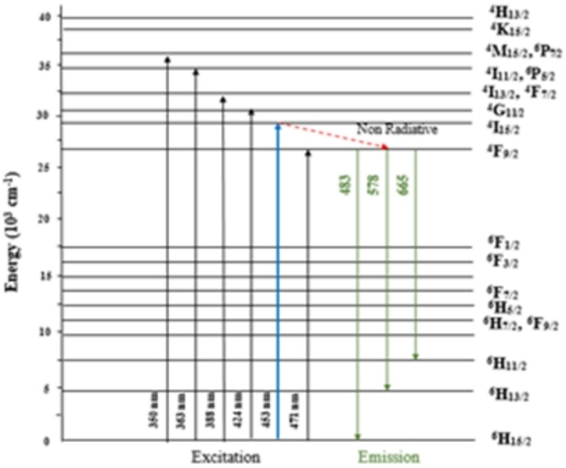

Figure 5: The diagram of partial energy levels of NaBaBiB:Dy^{3+} glasses [11, 12].

peaks corresponds to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^6H_{13/2}$ and $^6H_{11/2}$ transitions under 453 nm excitation. The optimal concentration of Dy_2O_3 in the NaBaBiB glasses was found to be 1.5 mol%.

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