

THE EFFECT OF BARIUM CONTENT ON THE LUMINESCENCE PROPERTY OF DYSPROSIUM-DOPED BORATE GLASSES

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Received: May 01, 2023; Revised: June 30, 2023; Accepted: August 14, 2023

Abstract

Barium sodium borate glasses doped with Dy₂O₃ were fabricated in this work with the variation of barium oxide concentration. The excitation spectra, with 575 nm emission, show the highest excitation band at 349 nm. The emission spectra, with 349 nm excitation, show the emission bands at 482 and 575 nm. The highest emission light yield has occurred when the glass sample has 10 mol% of BaO. The (x,y) color coordinates of the emitted light from all the glass samples were (0.37,0.41) that point at the white light region in the CIE 1931 color space. The Y/B ratio indicates a high asymmetric environment around Dy³⁺ ions. The luminescence lifetimes are found to be 0.455 for all the glass samples.

Keywords: Borate Glass; Dysprosium; Photoluminescence

Introduction

Nowadays, LEDs (light-emitting diodes) are commonly used as white light lamps for all residential, commercial, and industrial, because of several advantages over traditional incandescent or fluorescent lamps, including, energy efficiency, long lifespan, durability, design flexibility, and safety. LEDs can emit white light through a process involves using a blue LED chip coated with a phosphor material that absorbs some of the blue light before re-emits it as a mixture of colors that

appear as white light. The phosphor material used in white LEDs typically consists of a rare earth element, such as cerium (Ce), yttrium (Y), or terbium (Tb), along with other compounds. When blue light from the LED chip passes through the phosphor material, it excites the electrons in the rare earth element, causing them to emit light at longer wavelengths in the red, green, or red. The resulting combination of blue and longer-wavelength light appears as white light to the human eye.

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DOI: <https://doi.org/10.55766/sujst-2023-05-e02783>

Suranaree J. Sci. Technol. 30(5):030142(1-6)

Alternatively, white LEDs can also be created by combining multiple-colored LEDs, such as red, green, and blue, in a single package. This approach is known as RGB (red, green, blue) LED technology (Chiu *et al.*, 2007; Kim *et al.*, 2012; Rasool *et al.*, 2013; Mishra *et al.*, 2016).

Dy³⁺ (dysprosium) is a rare earth element that can be incorporated into glass to impart unique optical properties, including white LED, solid-state laser, and optical amplifier. Dy³⁺-doped glass can be used in LEDs (light-emitting diodes) as an efficient phosphor to convert blue or UV light into white light. The process of using Dy³⁺-doped glass in LEDs involves exciting the Dy³⁺ ions with blue or UV light, which causes them to emit light at longer wavelengths in the visible spectrum, typically in the white region. Host glass for doping Dy³⁺ ions can be further improved for more efficiency, high brightness, excellent color rendering, and color quality of LEDs (Chiu *et al.*, 2007; Kim *et al.*, 2012; Rasool *et al.*, 2013; Mishra *et al.*, 2016).

Barium sodium borate glass is selected for doping with Dy³⁺ ions in this work. Barium can act as a glass modifier that can affect the properties of the glass. Barium ions with a larger ionic radius can break or distort the B-O-B bonds in the glass system, resulting in the new formation of Ba-O-B bonds (Tripathi *et al.*, 2006; Rajesh *et al.*, 2012; Jayasankar *et al.*, 2013; Moorthy *et al.*, 2013; Dawauda *et al.*, 2014; Shanmugavelu and Kumar, 2014). This can alter the glass network structure, affecting many properties of the glass, such as the physical, optical, and luminescence properties. This study investigated the impact of varying Ba₂O₃ concentrations on the properties of Dy³⁺-doped Ba-Na-B glasses, aiming for improving the performance and efficiency of the glass samples for use as white LEDs.

Experimental Details

The fabrication of Dy³⁺-doped barium sodium borate glass with varying barium concentrations can be achieved through the melt-quenching technique, which involves melting the required components together, followed by quenching the molten mixture to form a glass. The chemical compositions are

$x\text{BaO}:25\text{Na}_2\text{O}:(74-x)\text{B}_2\text{O}_3:1\text{Dy}_2\text{O}_3$, BaO concentrations chosen for study in this work are 5, 10, 15, and 20 mol%. The required components for the glass fabrication are Dy₂O₃, BaCO₃, Na₂CO₃ and H₃BO₃. The Dy₂O₃ is the source of Dy³⁺ ions in the glass samples. The varying concentration of barium can be achieved by adjusting the amount of BaCO₃ used. The fabrication process involves mixing the required components in the desired ratio and melting them in a high-temperature furnace at the temperature of 900°C for 3 hours. After the samples were melted, the molten mixture was quenched rapidly to form a glass before annealing by moving the glasses to an annealing furnace for annealing at the temperature of 500°C for 3 hours. The resulting glasses were cut to 1.0×1.5×0.3 cm³ dimensions that were suitable for use in the instruments in this research. The glasses were also polished to remove any surface imperfections, such as scratches, roughness, or irregularities introduced during the cutting process. A smooth glass surface is crucial to enhance the optical properties of the glass by improving light transmission and reducing light loss due to scattering. Then the glasses can be characterized using various techniques to determine their physical, optical, and photoluminescence properties.

The density of the glasses was calculated by the following method: 1) Weighting the glasses in air using a 4-digit microbalance. 2) A beaker filled with distilled water was placed on the balance and the samples were submerged in the water. The weight of the displaced water was then measured. 3) The density was calculated by the Archimedes' method. Abbe refractometer (ATAGO, NAR-3T) was used for investigating the refractive index with a sodium D line of 589 nm. The absorption spectra were measured by Shimadzu, UV-3600 UV-Vis-NIR spectrophotometer. The photoluminescence properties were obtained using Agilent, Cary Eclipse fluorescence spectrophotometer. All the measurements were evaluated at room temperature.

Results and Discussions

Table 1 shows each glass composition, varying the BaO concentrations from 5, 10, 15, and 20 mol%,

Table 1. Density, molar volume, and refractive index

Glass compositions	Symbol	Density (g/cm ³)	Molar volume (cm ³ /mol)	Refractive index
5BaO:25Na ₂ O:69B ₂ O ₃ :1Dy ₂ O ₃	5Ba:Dy	2.5534	29.3448	1.5512
10BaO:25Na ₂ O:64B ₂ O ₃ :1Dy ₂ O ₃	10Ba:Dy	2.7924	28.3320	1.5520
15BaO:25Na ₂ O:59B ₂ O ₃ :1Dy ₂ O ₃	15Ba:Dy	2.9723	28.0253	1.5541
20BaO:25Na ₂ O:54B ₂ O ₃ :1Dy ₂ O ₃	20Ba:Dy	3.1876	27.4454	1.5573

and their corresponding symbol, along with the density, molar volume, and refractive index. The results show a clear trend that when the BaO concentration increases, the density of the glass samples also increases, while the molar volume decreases, as shown in Figure 1. The increase in density with increasing BaO concentration can be attributed to the higher atomic mass of Ba compared to other glass constituents. The addition of BaO introduces more massive atoms into the glass structure, leading to an increase in overall mass and, consequently, density. Simultaneously, the molar volume decreases as the BaO concentration increases. This phenomenon suggests that the structural rearrangements induced by the presence of BaO result in a more compact and denser glass network. In general, there is a correlation between the refractive index and the density of a transparent material like glass. There is a tendency for the refractive index of glass to increase with increasing density. And the addition of BaO may lead to an increase in the polarizability of the glasses that causes the increasing in refractive index (Phongsa *et al.*, 2022; Ullah *et al.*, 2022). The results show that when BaO is introduced into the glass composition, it can influence the arrangement and bonding within the glass network, leading to structural modifications that affect these physical properties.

The absorption spectra in ultraviolet-visible regions and near-infrared regions are shown in Figures 2 and 3, respectively. The absorption bands

are corresponding to electronic transitions between different energy levels of the Dy^{3+} ions, starting from $^6\text{H}_{15/2}$ to $^6\text{P}_{7/2}$, $^4\text{K}_{17/2}$, $^4\text{G}_{11/2}$, and $^4\text{I}_{15/2}$ in UV-Vis regions, corresponding to the wavelength at 349, 387, 426, and 452 nm, respectively. And the transitions starting from $^6\text{H}_{15/2}$ to $^6\text{F}_{3/2}$, $^6\text{F}_{5/2}$, $^6\text{F}_{7/2}$, $^6\text{F}_{9/2}$, $^6\text{H}_{9/2}$ and $^6\text{H}_{11/2}$ in NIR region, corresponding to the wavelength at 749, 795, 886, 1079, 1259 and 1659 nm, respectively (Som and Karmakar, 2011; Reddy *et al.*, 2015; Phongsa *et al.*, 2022; Ullah *et al.*, 2022). Changes in the BaO content of the glass potentially affect the intensity of the absorption spectra. BaO dopant ions introduce energy levels within the glass matrix that can interact with incident photons. As the BaO concentration increases, the number of these energy levels may increase, enhancing the absorption of light within the glass. Furthermore, the addition of BaO may induce structural modifications in the glass network, such as the formation of clusters or the enhancement of cross-linking between atoms. These structural changes can result in variations in the electronic states of the glass, which may lead to an increased absorption intensity.

The excitation spectra (Figure 4) were obtained by investigating the emission intensity of the Dy^{3+} ions at 575 nm emission wavelength, while varying the excitation wavelength. The excitation spectra with excitation bands that belonged to the transitions from $^6\text{H}_{15/2}$ to $^4\text{M}_{17/2}$, $^6\text{P}_{7/2}$, $^6\text{P}_{5/2}$, $^4\text{K}_{17/2}$, $^4\text{G}_{11/2}$, $^4\text{I}_{15/2}$ and $^4\text{F}_{9/2}$ at 324, 349, 363, 386, 424, 453

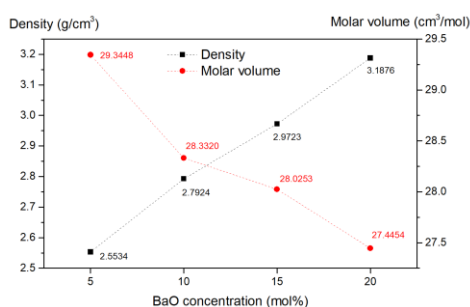


Figure 1. The density and molar volume

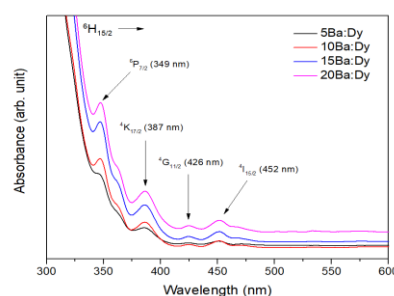


Figure 2. The absorption spectra in the UV-Vis region

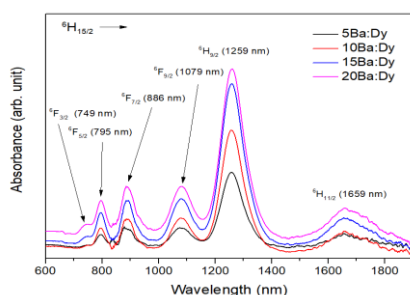


Figure 3. The absorption spectra in NIR region

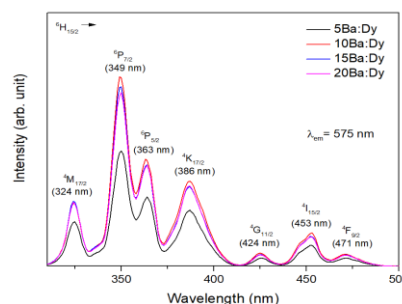


Figure 4. The excitation spectra

and 471, respectively. The greatest excitation band belongs to the ${}^6\text{H}_{15/2} \rightarrow {}^6\text{P}_{7/2}$ electronic transition at 349 nm.

The emission spectra of Dy^{3+} -doped glasses, excited with 349 nm, revealed several distinct emission bands. These emission bands correspond to specific energy transitions within the Dy^{3+} electronic structure with 2 important bands at 482 nm (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$) and 575 nm (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$) and other 2 minor bands at 665 nm (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$) and 753 nm (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{9/2}$), as shown in Figure 5. The observed emission bands were analyzed and compared with known energy levels and transitions of Dy^{3+} (Som and Karmakar, 2011; Reddy *et al.*, 2015; Phongsa *et al.*, 2022; Ullah *et al.*, 2022). The energy level transition mechanism of Dy^{3+} ions is shown in Figure 6. As the increasing of BaO concentrations from 0 to 10 mol%, the intensity increased, indicating enhanced excitation and emission efficiency. However, as the Ba concentration was further increased beyond 10 mol%, the band intensity began to decrease. The maximum excitation and emission band intensities were observed at a Ba concentration of 10 mol% (10Ba:Dy glass). The quenching effect was attributed to the transformation of BO_3 to BO_4 when Ba is added to the borate glass composition. The conversion from BO_3 to BO_4 increases as the amount of BaO increases up to 10 mol%. However, if more BaO is added beyond this point, it converts BO_4 back to BO_3 (Phongsa *et al.*, 2022; Ullah *et al.*, 2022). Consequently, the 10Ba:Dy glass contains the most BO_4 structures, resulting in the highest efficiency in terms of excitation and emission.

The relative intensity of the major bands at 575 and 482 nm in the emission spectra can depend on several factors, including the environment around the Dy^{3+} ions in a glass network (Phongsa *et al.*, 2022; Ullah *et al.*, 2022). Dy^{3+} ions exhibit strong

yellow and blue emission bands, which are attributed to the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ (575 nm, yellow) and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ (482 nm, blue) transitions, respectively. The yellow/blue ratio (Y/B ratio) in the emission spectra of Dy^{3+} ions can be used to provide information about the asymmetry characteristic that can affect the photoluminescence properties of the Dy^{3+} ions in the host glass. In general, the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transition (provides emission in yellow color) is an electric dipole transition, while the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ transition (provides emission in blue color) is a magnetic dipole transition. The electric dipole transition involves a change in the electron distribution within the 4f subshell of the RE^{3+} ions that is allowed because of the asymmetry around the RE^{3+} ions. While the magnetic dipole transition involves a change in the magnetic moment of the RE^{3+} ions that are not involved with the environment around the RE^{3+} ions. So, if the Dy^{3+} ions are surrounded by a highly asymmetric environment, the yellow emission intensity will be greater than the blue emission intensity, resulting in a higher Y/B ratio.

In conclusion, the Y/B ratio can provide valuable information about the symmetry of the coordination environment around Dy^{3+} ions, a higher Y/B ratio suggests a more asymmetry environment, that may lead to a stronger luminescence efficiency. On the other hand, a lower Y/B ratio indicates a more symmetric environment, that may cause a weaker luminescence efficiency. In this work, the Y/B ratio values are 1.48, 1.65, 1.54, and 1.63 for the glasses with 5, 10, 15, and 20 mol% of BaO, respectively.

The result indicates a significant asymmetry in the environment surrounding the Dy^{3+} ions. To describe the color of the light from the emission according to the CIE 1931 color space, the emission spectra data were used to calculate the

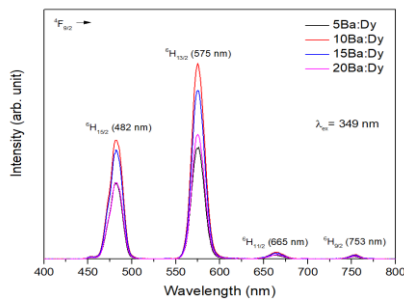


Figure 5. The emission spectra

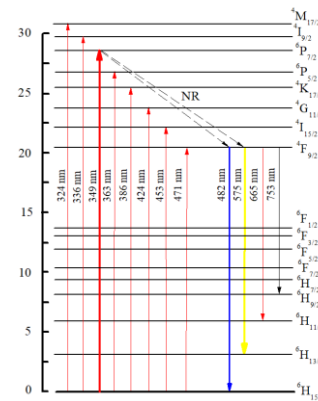


Figure 6. Energy level scheme for the emission mechanism

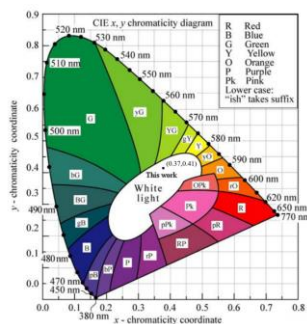


Figure 7. The CIE 1931 chromaticity diagram

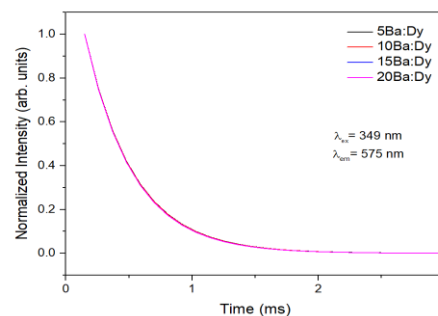


Figure 8. The luminescence decay curve

corresponding chromaticity coordinates. In this work, the (x,y) chromaticity coordinates of all the glasses are all located at (0.37,0.41) in the white region (Figure 7).

The investigation involved examining the decay curve by first exciting it at 349 nm and then observing the emitted light over a period of time, specifically focusing on the 575 nm wavelength of emission. The luminescence decay curve is presented in Figure 8. To determine the luminescence lifetime, the curve was fitted to an exponential decay function using standard curve-fitting techniques. The calculated lifetimes for all samples were found to be 0.455 ms, without taking into account the influence of the added BaO concentration in the glass samples.

Conclusions

Dy³⁺-doped barium sodium borate glasses were produced by incorporating 5, 10, 15, and 20 mol%. The glass containing 10 mol% BaO demonstrated the highest excitation and emission intensities. In terms of color, the (x,y) chromaticity coordinates for this glass were measured at (0.37,0.41) within the white region of the CIE 1931 color space. The Y/B ratio values for the 5Ba:Dy, 10Ba:Dy, 15Ba:Dy, and 20Ba:Dy glasses were determined as 1.48, 1.65, 1.54, and 1.63, respectively, indicating a significant asymmetry in the environment surrounding the Dy³⁺ ions. The lifetimes of all samples were found to be 0.455 ms, without considering the influence of BaO concentration in the glass samples. These results demonstrate the potential of the Dy³⁺-doped glasses developed in this study for application in efficient white LEDs, highlighting their performance and effectiveness.

Acknowledgments

The authors express the gratitude to Suan Sunandha Rajabhat University (SSRU) and the Center of Excellence in Glass Technology and Materials Science (CEGM) at Nakhon Pathom Rajabhat University (NPRU) for providing support during the course of this research.

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