Study on Judd-Ofelt theory for Er$^{3+}$ and Yb$^{3+}$ doped tungsten gadolinium borate glasses for NIR lighting application

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Abstract. The tungsten gadolinium borate glass doped with Er$^{3+}$ and co-doped with Er$^{3+}$/Yb$^{3+}$ were prepared by melt quenching technique to study the absorption, Judd-Ofelt theory, and luminescence properties. The glass composition (30-x) B$_2$O$_3$ - 42.5 WO$_3$ - 27.5 Gd$_2$O$_3$ - xEr$_2$O$_3$ (where x = 0.1 mol %) and (30-x-y) B$_2$O$_3$ - 42.5 WO$_3$ - 27.5 Gd$_2$O$_3$ - xEr$_2$O$_3$ - yYb$_2$O$_3$ (where x = 0.1 mol % and y = 1.0 mol %). The absorption spectra display the absorption peaks of the samples correspond with Yb$^{3+}$ and Er$^{3+}$ in the glass network, and the spectral parameters of each absorption and emission peaks were calculated using the Judd-Ofelt theory. NIR photoluminescence under 978 nm excitation was measured of glass in the region 1400-1700 nm. NIR emission display a peak centered at 1543 nm. This research is available for tunable laser and conventional-length optical amplifier.

Keywords: Borate glass, Judd-Ofelt theory, Luminescence.

1. Introduction

Nowadays, rare-earth ion-doped glasses have been widely studied. Since the great capacity for forming glass and a wide range of application within the various RE doped oxide glasses has been synthesized and distributed such as borates, silicates, tellurites, and phosphates [1,2]. Borate glasses is a particularly suitable optical material because of its high thermal stability, numerous coordination numbers, high RE ion solvency, relatively low melting point, and high clarity [3]. The Judd-Ofelt (JO) theory is one of the maxima successful theories for estimating the dimension of the forced electric dipole transition of the rare-earth ion. Standard J-O analyzes were applied to the room temperatures absorption spectrum of Er$^{3+}$ to determine the optical intensity parameter and radiative transitions probability.

Among rare earth, erbium or Er$^{3+}$ is one of the most attractive compositions with a widespread range of applications in telecommunications and optoelectronics, in particular, Er and Er / Yb doped glass with a wide emission of near-infrared radiation has potential application in the waveguide, optical fiber, and tunable laser. Yb$^{3+}$ has a large absorption cross-section, resulting in good spectral overlap with Er$^{3+}$ transition, thus enabling efficient Yb$^{3+}$-Er$^{3+}$ energy transfer [4]. Due to the efficient transfer of energy from Gd$^{3+}$ ion to the luminescence activator, high-heat neutrons capture the cross-section and increase the emission of light. Tungsten is important due to decrease phonon in the glass and increased density [5]. This research has been preparation tungsten gadolinium borate glass doped Er$^{3+}$ ions and co-doped Er$^{3+}$/Yb$^{3+}$ to study the optical, luminescence properties, and Judd-Ofelt (JO) theory.

2. Experimental

Er$_2$O$_3$ doped tungsten gadolinium borate glass with a chemical compositions of (30-x) B$_2$O$_3$ - 27.5 Gd$_2$O$_3$ - 42.5 WO$_3$ - xEr$_2$O$_3$ (where x = 0.1 mol%) and Er$_2$O$_3$/Yb$_2$O$_3$ co-doped tungsten gadolinium borate glass with a chemical compositions of (30-x-y) B$_2$O$_3$ - 27.5 Gd$_2$O$_3$ - 42.5 WO$_3$ - xEr$_2$O$_3$ -
yYb,O₃ (where x = 0.1 mol% and y = 1.0 mol%) have been manoeuvre by the melt quenching technique. The chemical mixed in a mortar and homogeneous mixes were taken up in an alumina crucible weighing 10 g. Melted it in an electric furnace at 1200 °C for 3 hours, the melting is poured over a preheaters graphite mold and annealed for 3 hours at 500 °C to dispose of heat stress then cooled to room temperatures. These glasses sample were subsequently polished for optical measurements for accuracy transparency and flat surfaces. Figure 1 display the glass samples from this work.

![Figure 1](image)

Figure 1. Photograph of Er³⁺/ Er³⁺-Yb³⁺ doped/co-doped B₂O₃ - Gd₂O₃ - WO₃ glass

The density of glass (ρ) was measured as shown by Eq.1’s Archimedes law, where the sample of glass was weighed as an immersed liquid in the air (wₐ), water (wₕ) and ρₕ is the density of water (1 g/cm³).

\[
\rho = \frac{wₐ}{wₐ - wₕ} \times ρₕ
\]

The molar volume (Vₘ) calculation is display by Eq. 2 corresponding to the density of the glasses, where \( M_T \) is the maximum molecular weight of several components within the glasses.

\[
Vₘ = \frac{M_T}{ρ} \tag{2}
\]

A UV-Vis-NIR spectrophotometer (Shimadzu UV-3600) in the wavelength range of 200-2500 nm was used to analyze absorption spectra. A fluorescence spectrometer (Cary-Eclipse) and photoluminescence spectrometer (PTL, Quantum Master-300) were used to record the excitation, emission. At room temperature, all measures are completed.

3. Results and Discussion

3.1 Physical properties

From the study of the density, molar volume, and refractive index of doped Er³⁺ and co-doped Er³⁺-Yb³⁺. Table 1. found that the density of co-doped Er³⁺-Yb³⁺ is higher than the doped Er³⁺, by co-doped Er³⁺-Yb³⁺ has a density equal to 6.0691 g/cm³. While the doped Er³⁺ has a density equal to 6.0332 g/cm³. The molar volume of co-doped Er³⁺-Yb³⁺ is greater than the doped Er³⁺, by co-doped Er³⁺-Yb³⁺ has a molar volume equal to 36.888 cm³/mol. While the doped Er³⁺ has a molar volume equal to 36.3692 cm³/mol [6]. And found that the refractive index of co-doped Er³⁺-Yb³⁺ is higher than the doped Er³⁺, by co-doped Er³⁺-Yb³⁺ has equal to 1.6081. While the doped Er³⁺ has equal to 1.5255.

| Physical properties | WGBEr | WGBEr/Yb |
|---------------------|-------|----------|
| Density             | 6.0332| 6.0691   |
| Molar volume        | 36.3692| 36.6888  |
| Refractive index    | 1.5255| 1.6081   |
3.2 Optical absorption spectra

Results from the absorptions spectra study of borate glasses doped with Er₂O₃ and Yb₂O₃ are display in Figure 2. Er₂O₃ and Yb₂O₃ doped borate glasses were found to absorb light from visible wavelengths to near-infrared. The entire eight absorption band corresponding to Er³⁺ absorption are excitation from the ground states \(^4I_{15/2}\) to excited state \(^2F_{7/2}\) (450 nm), \(^4F_{9/2}\) (488 nm), \(^2H_{11/2}\) (524 nm), \(^4S_{3/2}\) (544 nm), \(^4F_{9/2}\) (654 nm), \(^4I_{15/2}\) (802 nm), \(^4I_{11/2}\) (978 nm), and \(^4I_{13/2}\) (1529 nm) respective. In addition, the absorption peak of Yb³⁺ overlaps with Er³⁺ at a wavelength of 978 nm. Changes in energy levels from ground state \(^2F_{7/2}\) to \(^2F_{5/2}\), where the peak absorption at 978 nm is best. Such absorption causes the change in the energy levels of Yb³⁺ and Er³⁺ from the ground states to the excited state \(^2F_{7/2}\) \(\rightarrow\) \(^2F_{5/2}\) (978 nm) and \(^4I_{15/2}\) \(\rightarrow\) \(^4I_{11/2}\) (978 nm) respectively [7]. Yb³⁺ has a large absorption cross-section, resulting in good spectral overlap with Er³⁺ transitions, thus making Yb³⁺ - Er³⁺ energy transfer efficient [4]. And the Er₂O₃ doped borate glass absorption spectra showed that Er³⁺ absorption spectra consisted of light at 450, 488, 524, 544, 654, 802, 978, and 1529 nm.

![Absorption Spectra](image)

**Figure 2.** Absorptions spectra of Er³⁺/Er³⁺:Yb³⁺ doped/co-doped B₂O₃ - Gd₂O₃ - WO₃ glass in UV visible and NIR regions

3.3 Excitation spectra

The study found that borate glass doped Er₂O₃ and Yb₂O₃ emit 1543 nm wavelength. The researcher then further studied the light used to stimulate the glass. The glass was then emitted at 1543 nm by measuring the excitation spectra display in Figure 3. It was found that a wavelength of 275 nm stimulated the glass, causing Gd³⁺ to transitions from the ground state to the excitation state \(^4S_{9/2}\) \(\rightarrow\) \(^4I_{15/2}\) (275 nm). And cause Er³⁺ to transitions from ground state to excitations state \(^4I_{15/2}\) \(\rightarrow\) \(^2G_{7/2}\) (350 nm), \(^4G_{9/2}\) (369 nm), \(^4G_{11/2}\) (380 nm), \(^4G_{9/2}\) (408 nm), \(^4F_{5/2}\) (450 nm), \(^4F_{7/2}\) (448 nm), \(^2H_{11/2}\) (524 nm), \(^4S_{3/2}\) (545 nm), \(^4F_{9/2}\) (654 nm), \(^4I_{15/2}\) (802 nm) and \(^4I_{11/2}\) (978 nm). A wavelength of 978 nm stimulated into the glass causes Yb³⁺ transitions from the ground state to excitations states \(^2F_{7/2}\) \(\rightarrow\) \(^2F_{5/2}\). The researcher selected a peak to stimulate the glass at a wavelength of 975 nm because it was an activation peak of both Er³⁺ and Yb³⁺. When comparing glasses between Er₂O₃-doped borate glass and Er₂O₃ and Yb₂O₃-doped borate glass. It was found that the borate glass peaks doped with Er₂O₃ and Yb₂O₃ had higher light intensity [7].
3.4 NIR photoluminescence analysis
From the stimulation spectra previously mentioned the researcher then took the peak wavelength at 978 nm to study the emitting spectra, display in Figure 4. It was found that borate glass doped Er₂O₃ and Yb₂O₃ emit light at a wavelength of 1543 nm. When comparing glasses between Er₂O₃-doped borate glass and Er₂O₃ and Yb₂O₃-doped borate glass. It was found that the borate glass peaks doped with Er₂O₃ and Yb₂O₃ had higher light intensity since Yb³⁺ acts as the role of sensitizer absorb 978 nm light in WGBEr/Yb glass. The glass undergoes a transition from the Er³⁺ and Yb³⁺ layers from the ground states to the excitation state ⁴I₁₅/₂ → ⁴I₁₁/₂ and ⁡F₇/₂ → ⁡F₅/₂ respectively. After that Yb³⁺ then transfers energy to Er³⁺ from ⁡F₅/₂ → ⁴I₁₁/₂. After that, there was a reduction in the energy class non-radiative relaxation down to state ⁴I₁₃/₂. Later it emits light at the energy level ⁴I₁₃/₂ → ⁴I₁₅/₂ (1543 nm) [8,9].

![Figure 3. Excitation spectra of Er³⁺/Er³⁺-Yb³⁺ doped/co-doped B₂O₃ - Gd₂O₃ - WO₃ glasses.](image)

![Figure 4. Near infrared emissions spectra (λex = 978 nm) of Er³⁺/Er³⁺-Yb³⁺ doped/co-doped B₂O₃ - Gd₂O₃ - WO₃ glasses](image)

![Figure 5. Energy transfer diagram of Er₂O₃ and Yb₂O₃ doped glass](image)
3.5 Judd-Ofelt Analysis
The researcher has led the borate glass doped with Er<sub>2</sub>O<sub>3</sub> and borate glass co-doped with Er<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> was analyzed the light-emitting properties using J-O theory. This starts with taking the area under the peak spectral light absorption and the refractive index of such glasses, it was used to find the f<sub>exp</sub> (expressed oscillator strength) value from the equation in the paper [10-12]. And later the f<sub>cal</sub> (calculated oscillator strength) was used to find the Ω<sub>2</sub>, Ω<sub>4</sub>, and Ω<sub>6</sub> from the equation in the paper [17-18]. It is displayed in Table 2. The highest oscillator strength belongs to the 4I<sub>15/2</sub>→2H<sub>11/2</sub> transition due to the best absorption at 524 nm in absorption spectra. Which is equal to 8.9978×10<sup>-6</sup> cm<sup>2</sup>, 9.0290×10<sup>-6</sup> cm<sup>2</sup>, 10.9471×10<sup>-6</sup> cm<sup>2</sup> and 10.9763×10<sup>-6</sup> cm<sup>2</sup> respectively. Along with δ<sub>rms</sub> (root mean square deviation) to determine the quality of the fit between the f<sub>exp</sub> and f<sub>cal</sub> values of the absorption transition. And the deviation of δ<sub>rms</sub> was found to be ± 0.716 and 0.909. The J-O parameters (Ω<sub>2</sub>, Ω<sub>4</sub>, Ω<sub>6</sub>) It was found that borate glass co-doped with Er<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> had higher Ω<sub>2</sub>, Ω<sub>4</sub>, and Ω<sub>6</sub> values than borate glass doped with Er<sub>2</sub>O<sub>3</sub>. Are display in Table 3, borate glass doped with Er<sub>2</sub>O<sub>3</sub> Ω<sub>2</sub> = 6.404×10<sup>-20</sup> cm<sup>2</sup>, Ω<sub>4</sub> = 0.989×10<sup>-20</sup> cm<sup>2</sup> and Ω<sub>6</sub> = 1.574×10<sup>-20</sup> cm<sup>2</sup> and borate glass co-doped with Er<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> Ω<sub>2</sub> = 7.871×10<sup>-20</sup> cm<sup>2</sup>, Ω<sub>4</sub> = 0.236×10<sup>-20</sup> cm<sup>2</sup> and Ω<sub>6</sub> = 1.419×10<sup>-20</sup> cm<sup>2</sup>. The J-O parameters of borate glass doped with Er<sub>2</sub>O<sub>3</sub> and borate glass co-doped with Er<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> follow the trend as Ω<sub>2</sub> > Ω<sub>6</sub> > Ω<sub>4</sub>, which is the same as the trend observed in many Er<sup>3+</sup>/Er<sup>3+</sup>-Yb<sup>3+</sup>doped/co-doped glasses [11,12]. The value of Ω<sub>2</sub> signifies strong covalent bonding at the optimum doping level. In addition, the Ω<sub>4</sub> and Ω<sub>6</sub> parameter represent a low sensitivity to changes in the Er<sup>3+</sup> ion environment [13,14].

Table 2. Absorption spectra position, f<sub>exp</sub> and f<sub>cal</sub>(×10<sup>-6</sup>) of WGBEr and WGBEr/Yb glasses

| Transition  | f<sub>exp</sub> | f<sub>cal</sub> |
|-------------|----------------|--------------|
| 4I<sub>15/2</sub>→2F<sub>5/2</sub> | 0.8607 | 0.4587 | 0.7218 | 0.6934 |
| 4I<sub>15/2</sub>→2F<sub>7/2</sub> | 1.2754 | 1.0616 | 2.1438 | 1.8651 |
| 2H<sub>11/2</sub> | 8.9978 | 10.9471 | 9.0290 | 10.9763 |
| 4S<sub>3/2</sub> | 2.9130 | 2.3154 | 0.5914 | 0.5682 |
| 4F<sub>9/2</sub> | 2.0579 | 1.2570 | 1.7764 | 1.1777 |
| 4I<sub>9/2</sub> | 0.2000 | 0.4143 | 0.2156 | 0.0676 |
| 2H<sub>11/2</sub> | 1.3447 | 1.2588 | 0.7592 | 0.7888 |
| 4I<sub>13/2</sub> | 1.3542 | 1.3581 | 1.5081 | 1.4256 |
| δ<sub>rms</sub> | 0.716 | 0.909 |

Table 3. Comparisons of J-O parameter (×10<sup>-20</sup> cm<sup>2</sup>) of WGBEr and WGBEr/Yb glasses with previous research

| Glasses | Ω<sub>2</sub> | Ω<sub>4</sub> | Ω<sub>6</sub> | Ω<sub>2</sub> > Ω<sub>6</sub> > Ω<sub>4</sub> |
|---------|-------------|-------------|-------------|-----------------------------------|
| WGB:0.1Er | 6.404 | 0.989 | 1.574 | Ω<sub>2</sub> > Ω<sub>6</sub> > Ω<sub>4</sub> |
| WGB:0.1Er/1Yb | 7.871 | 0.236 | 1.419 | Ω<sub>2</sub> > Ω<sub>6</sub> > Ω<sub>4</sub> |
| 0.5Er [11] | 4.980 | 2.530 | 2.150 | Ω<sub>2</sub> > Ω<sub>6</sub> > Ω<sub>4</sub> |
| 0.5Er/1Yb [11] | 4.980 | 1.710 | 2.230 | Ω<sub>2</sub> > Ω<sub>6</sub> > Ω<sub>4</sub> |
| PG:0.25Er/1Yb [12] | 4.120 | 1.330 | 1.470 | Ω<sub>2</sub> > Ω<sub>6</sub> > Ω<sub>4</sub> |
| PBN:0.1Er [13] | 1.283 | 2.501 | 6.237 | Ω<sub>6</sub> > Ω<sub>2</sub> > Ω<sub>4</sub> |
| PBN:0.1Er/0.1Yb [13] | 3.786 | 2.698 | 5.860 | Ω<sub>6</sub> > Ω<sub>2</sub> > Ω<sub>4</sub> |
Table 4. displays WGBEr and WGBEr/Yb (λex = 978 nm) glass were assessed using the JO parameter obtained from the absorption spectra measurement. $A_R$ is radiative transition probabilities, $\beta_R$ is luminescence branching ratios, and the value of the emission cross-section ($\sigma_e$) represents the energy extraction rate from the optical material and is an important parameter for the glasses material to act as a good fluorescent host material [20]. When considering the value of both glasses, it can be seen that glass co-doped with Yb$_2$O$_3$ can increase the efficiency of using glass to be more laser. So, borate glass co-doped with Er$_2$O$_3$ and Yb$_2$O$_3$ is a material with high potential. Suitable for use as a lasers media in solid lasers emitting wavelength 1543 nm [12,14-16].

Table 4. Emission peak wavelength (λP), $A_R$, $\beta_R$ and $\sigma_e$ for the observed emission transition of WGBEr and WGBEr/Yb

| Transition | $\lambda_P$ (nm) | $A_R$ (s$^{-1}$) | $\beta_R$ | $\sigma_e \times 10^{21}$ (cm$^2$) |
|------------|-------------------|-----------------|-----------|-----------------------------------|
| $^4I_{13/2}$ → $^4I_{15/2}$ | 1543 | 149.64 | 161.46 | 1 | 1 | 4.9365 | 4.9365 |

4. Conclusion

WGBEr and WGBEr/Yb glasses are transparent and pink. Both density, molar volume, and refractive index of co-doped Er$^{3+}$/Yb$^{3+}$ are greater than the doped Er$^{3+}$. The absorption spectra of the glasses have absorption in the range ultraviolet to the range near-infrared region. NIR luminescence spectra under 978 nm excitation wavelength of Er$^{3+}$/Er$^{3+}$-Yb$^{3+}$ doped/co-doped B$_2$O$_3$ - Gd$_2$O$_3$ - WO$_3$ glass. Display the NIR emission peak was centered at 1543 nm. Borate glass that is co-doped with Er$_2$O$_3$ and Yb$_2$O$_3$ has a higher peak. Borate glass co-doped with Er$_2$O$_3$. The calculated Judd-Ofelt intensity parameter revealed a tendency of $\Omega_2 > \Omega_6 > \Omega_4$ of WGBEr and WGBEr/Yb glasses, the value of $\Omega_2$, in relation to the nearby structural change of the Er$^{3+}$ ions, represents the highest covalent environment of the Er$^{3+}$ ions in the B$_2$O$_3$ compound glasses. The low values of the $\Omega_4$ and $\Omega_6$ intensity parameters indicate lower strength and viscosity of the glasses host. The radiative properties of WGBEr and WGBEr/Yb glasses were predicted through the theory of JO. It can be seen that glass co-doped with Yb$_2$O$_3$ can increase the efficiency of using glass to be more laser. So, borate glass co-doped with Er$_2$O$_3$ and Yb$_2$O$_3$ is a material with high potential. Suitable for use as a lasers media in solid lasers emitting wavelength 1543 nm.

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References

[1] N. Jarucha, N. Wantana, T. Sareein, J. Kaewk Sao, Semiconductor Physics, Quantum Electronics & Optoelectronics. 2020; 23 (3). 276-281.
[2] S. Surendra Babu, H.J. Seo, C.K. Jayasankar, K.H. Jang, C.E. Jin, K. Jang, R. Rajeswari, J. Lumin. 2010; 130. 1021-1025.
[3] C.R. Kesavulu, H.J. Kim, S.W. Lee, J. Kaewk Sao, E. Kaewnuam, N. Wantana, J. Alloys and Compounds. 2017; 704. 557-564.
[4] G. Lakshminarayana, G.A. Kumar, I.V. Kityk, M.G. Brik, J. Qiu, J. Phys. Condens. Matter. 2008; 20. 375101.
[5] C.R. Kesavulu, H.J. Kim, S.W. Lee, J. Kaewk Sao, E. Kaewnuam, N. Wantana, J. Alloys Comp. 2017; 704. 557-564.
[6] H-R. BahariPoor, R. Zamiri, H.A. Aziz Sidek, J. Lumin. 2013; 143. 526-533.
[7] A. Pandey, K. Kumar, H.C. Swart, V. Kumar Rai, V. Kumar, Vi. Kumar, S. Som, Sensors and Actuators B. 2014; 202. 1305-1312.
[8] Y. Zhang, L. Zeng, J. Tang, H. Lei, Z. Xiao, J. Lumin. 2019; 212. 61-68.
[9] M. Li, J. Tang, K. Wang, X. Zhou, F. Jiang, Y. Zhang, J. Luan, Ceramics International. 2019; 45. 18831-18837.
[10] M.P. Hehlen, K.W. Kramer, M.G. Brik, J. Lumin. 2013; 136. 221-239.
[11] Y. Zhang, Ceramics International. 2018; 44. 22467-22472.
[12] Mingming Li, Ceramics International. 2019; 45. 18831-18837.
[13] N. Sdiri, J. Molecular Structure. 2012; 1010. 85-90.
[14] Y. Zhang, J. Tang, Z. Wu, W. Cao, J. Li, M. Li, Ceramics International. 2018; 44. 22467-22472.
[15] A.J. Barbosa, R.R. Goncalves, A.S.L. Gomes, S.R. Luthi, S.J.L. Ribeiro, Y. Messaddeq, F.A. Dias Filho, J. Non-Crystalline Solids. 2006; 352. 3636-3641.
[16] R. Reisfeld, K.A. Gschneidner Jr., C.K. Jorgensen, L. Eyring (Eds.), Elsevier Science. 1987; 58.