

OPTICAL AND NIR EMISSION OF Er^{3+} DOPED GADOLINIUM YTTRIUM ALUMINIUM GALLIUM BORATE GLASS FOR LASING MATERIAL

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Abstract

A series of Er^{3+} doped gadolinium yttrium aluminium gallium borate glass has been prepared by melt quenching technique for laser medium of infrared laser application and studied physical, optical, and luminescence properties of the effect of Er^{3+} concentration from 0.05 - 2 mol% in glass system. Physical properties such as density, and molar volume were studied by Archimedes' principle and calculated respectively. The density increases with increasing Er_2O_3 concentration due to degradation in the structure of the glass and B_2O_3 being replaced by high atomic weight in the glass network. The molar volume found that the trend increases with increasing Er_2O_3 concentration. Optical properties, the reflective index found the trend increases with increasing Er_2O_3 concentration, the absorption spectra were studied by UV-visible, NIR spectrophotometer, and luminescence properties were studied by fluorescence spectrophotometer. In the part of an optical property, the absorption spectra found the highest peak at 523 nm. The luminescence properties, the emission spectra found one peak at 1533 nm from the ground state ($^4\text{I}_{13/2}$) to excited state ($^4\text{I}_{15/2}$) by excitation at 523 nm. In addition, the emission spectra found one peak at 1558 nm from the ground state ($^4\text{I}_{13/2}$) to the excited state ($^4\text{I}_{15/2}$) when excitation by commercial laser at 980 nm. For the laser application, calculate by Judd-Ofelt theory.

Keywords: Borate; Luminescence; Erbium; Optical Materials; Gallium Borate Glasses

Introduction

In sedentary life, light has direct and indirect benefits to human beings, such as illuminating, beautiful, synthesizing vitamin D in the human body and electronic devices, etc. In modern times, optical knowledge and its application are rapidly

developing, giving rise to an overload of optical technologies, which affects the sedentary lifestyle (Kaewnuam *et al.*, 2017) Therefore, it is important to develop optical materials. This research uses glass as an optical material and focuses on laser

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media, because It's easy to prepare, low cost, transparency and can be improved by adding rare-earth oxide (Chanthima *et al.*, 2018). Er_2O_3 is doped into an NIR emitting glass system (BGEr glass) with the following elements: the B_2O_3 is the glass former and low melting point (Shofri *et al.*, 2020). Al_2O_3 can be modifier the glass structure (Lee *et al.*, 2015). These factors led to the study of BGEr glass doped with Er_2O_3 in the luminescence qualities for optical material. The cause of the light emitting of BGEr glass is caused by changing the energy level of Er^{3+} in glass structure from $^4\text{I}_{13/2}$ to $^4\text{I}_{15/2}$ and slight emission at 1533 (Zhang *et al.*, 2009). From the above studies, the $15\text{Ga}_2\text{O}_3$: $15\text{Al}_2\text{O}_3$: $10\text{Gd}_2\text{O}_3$: $10\text{Y}_2\text{O}_3$: $(50-x)\text{B}_2\text{O}_3$: $x\text{Er}_2\text{O}_3$ glass system (BGEr glass) (where $x = 0.00, 0.05, 0.10, 0.50, 1.00$ and 2.00 mol%) were designed and prepared by melt quenching technique. They were characterized by density, molar volume, refractive index, absorption spectra, excitation spectra, emission spectra, lifetime and Mccumber.

Experimentations

Glass preparation

The melt quenching procedure was used to create the BGEr glass with, the composition of $(50-x)\text{B}_2\text{O}_3$: $x\text{Er}_2\text{O}_3$: $15\text{Ga}_2\text{O}_3$: $10\text{Gd}_2\text{O}_3$: $15\text{Al}_2\text{O}_3$: $10\text{Y}_2\text{O}_3$ where $x = 0.00, 0.05, 0.10, 0.50, 1.00$ and 2.00 mol%. These oxides were melted at 1400°C for 3 hours and annealed at 500°C for 3 hours. For measurements, all glass was cut and polished to a size of $1.5 \times 1.0 \times 0.3$ cm.

Physical characteristics

At room temperature, the density (ρ) was calculated using Archimedes' technique. The total molecular weight (M_T) was divided by the density (ρ) to determine the molar volume (V_m).

The optical properties were measured as follows. The refractive index (n) of each sample was determined using an abbe refractometer and a sodium-vapour lamp with a light source 589 nm wavelength and monobromonaphthalene ($\text{C}_{10}\text{H}_7\text{Br}$), by model DR-M2. The optical absorption spectra were measured by UV-visible, NIR spectrophotometer (Shimadzu UV-3600) at 350 - 2500 nm of range. Finally, the fluorescence spectrophotometer (Agilent Cary-Eclipse) has a xenon lamp as an excitation source spectrum to measure the excitation, emission, and lifetime.

Results and Discussion

Physical characteristics

The density and molar volume characteristics of BGEr glasses are depicted in Figure 1 and Figure 2, respectively. The result of density found that the trend increases from 4.0478 to 4.2175 g/cm^3 with increasing of Er_2O_3 concentration from 0.05 mol% to 2 mol% due to degradation in the structure of the glass and Er_2O_3 (high 'Z' element) replaced by B_2O_3 (low 'Z' element) in the glass network as shown in Figure 1. The increase of Er_2O_3 as a result to molar volume increases due to breaking the network between borate and oxygen in glass structures or called non-bridging oxygen (NBO).

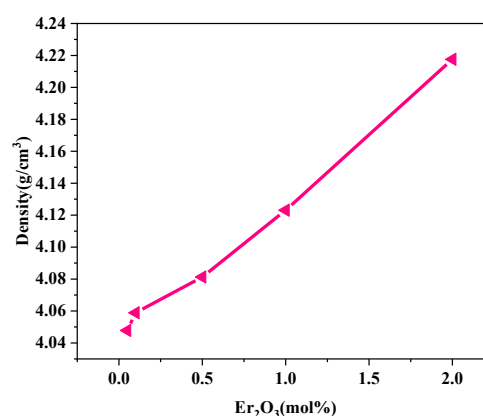


Figure 1. Density of BGEr glass doped with Er^{3+}

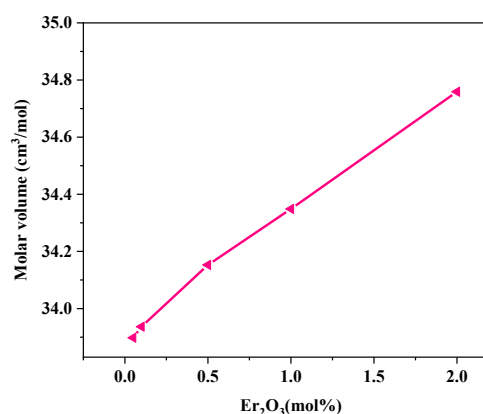


Figure 2. Molar volume of BGEr glass doped with Er^{3+}

Optical characteristics

Refractive index

The refractive index of BGEr glass increased from 1.6509 to 1.6517 with an increase in Er_2O_3 concentration from 0.05 mol% to 2 mol%. Slight discontinuity was observed at 0.5 mol%. Then, the refractive index increased beyond 1 mol%. An increase in the refractive index is due to the retardation of light with Er_2O_3 concentration and which involves breaking the network between borate and oxygen in glass structures as shown in Figure 3.

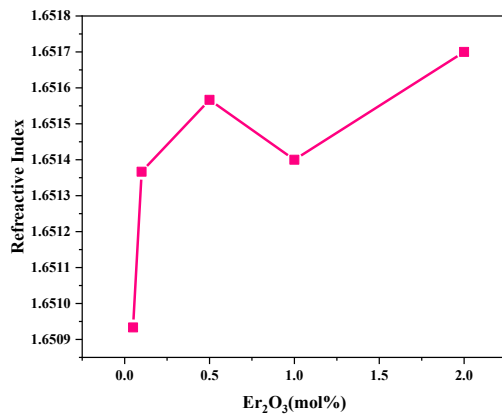


Figure 3. Refractive index of BGEr glass doped with Er^{3+}

Absorption spectra

At ambient temperature, the absorption spectra of Er_2O_3 doped glass were measured in the wavelength range of 300-1800 nm. These results are depicted in Figure 4. According to the absorption spectra's findings, the absorption peaks were in the UV-Vis-NIR region. In the range of UV, it is found that the peak is around 365, 380 nm, while in the range of visible light. It is found that the peak is around 408, 451, 489, 523, and 653 nm. In the range of NIR, it is found that the peak around 805, 979, and 1528 nm is observed, and discovered that the height of the peak increases when Er_2O_3 concentration increases from 0.05 mol% to 2 mol% (Zhang *et al.*, 2009). In Figure 4, the absorption bands peaked related to internal 4f-4f electronic transitions of Er^{3+} ions have been observed (ZHAO & SHI, 2013). The excited level of Er^{3+} corresponds to each assignment.

Luminescence characteristics

The emission spectra of Er_2O_3 glass in Figure 5 were measured by excitation at 523 nm. The emission of one peak was observed at 1533 nm

due to Er^{3+} ions. In addition, the Er_2O_3 glass was measured by excitation at 980 nm for commercial in Figure 6. The results found that the one emission peak at 1558 nm due to near-infrared emission changing the energy level of Er^{3+} ions. The excited state at $^4\text{I}_{13/2}$ to the ground state at $^4\text{I}_{15/2}$ due to Er^{3+} at the excited state has more energy than the ground state. It needs to release energy in the form of electromagnetic waves to match the energy of the ground state. The partial energy level diagram as shown in Figure 7, which corresponds to the NIR transition of the Er^{3+} ions doped in glasses, is a valuable resource for comprehending the dynamics at play in the excited state of the Er^{3+} ions.

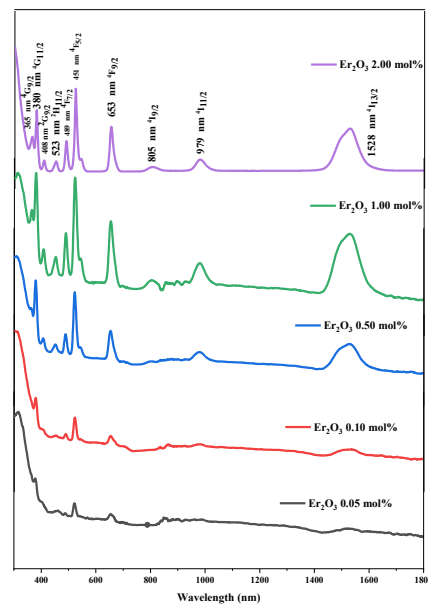


Figure 4. Absorption spectra of BG glass doped with Er^{3+}

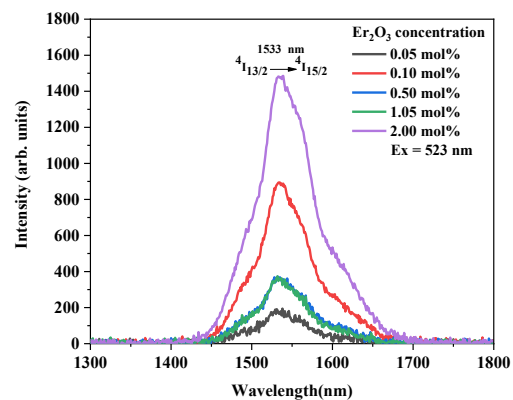


Figure 5. Emission spectra of BG glass doped with Er^{3+} (Excitation at 523 nm)

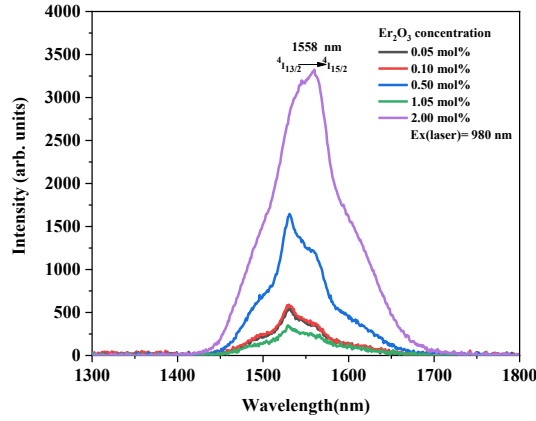


Figure 6. Emission spectra of BG glass doped with Er³⁺ (Excitation at 980 nm)

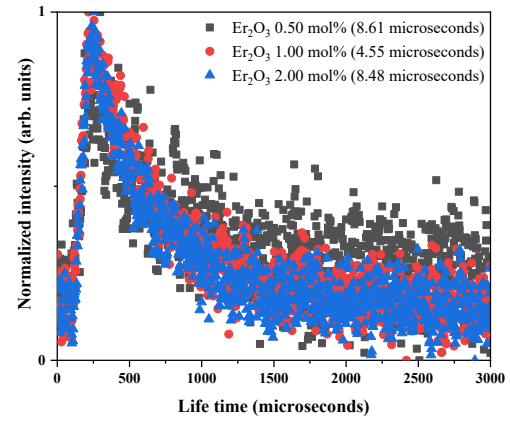


Figure 8. Lifetime of Er³⁺ of doped BG glass

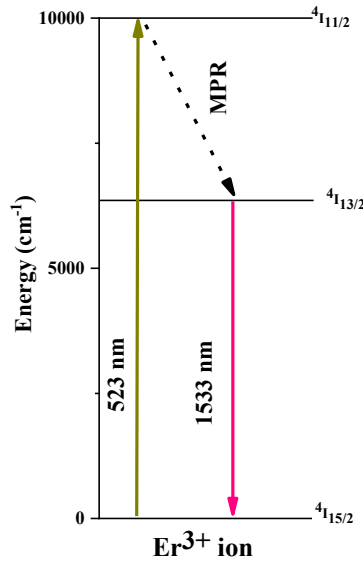


Figure 7. Level diagram of Er³⁺ doped glasses

Lifetime

The decay curve of the ⁴I_{13/2} excited level of Er³⁺ ions in BGxEr glasses stimulated at 980 nm is displayed in Figure 8. The lifetime of ⁴I_{13/2} excited level of Er³⁺ ions is an important parameter for designing an optical amplifier used in telecommunications and lasing material. The result shows the trend lifetime decrease because of the increase of Er₂O₃ concentration. The lifetime values have been estimated using the expressions reported in the literature (Mariyappan *et al.*, 2016) and for the ⁴I_{13/2} excited level the values are found to be 8.16, 4.45, and 8.48 μs for the prepared BGEr0.5, BGEr1.0, and BGEr2.0 glasses respectively.

Absorption, emission cross-section and optical gain characteristics of 1.53 μm band

As an important factor affecting the possible laser performance, the emission cross-section is measured using the absorption spectra and McCumber theory, respectively. This allowed for a better comprehension of the NIR ⁴I_{13/2} → ⁴I_{15/2} transition of the Er³⁺ ions in the glasses with the roles. Devices such as optical fiber lasers and lasing materials rely on the material's absorption and emission cross-section. The spectrum overlap of the absorption and emission cross-section is explained by McCumber's theory, which describes absorption data at 1533 nm. The broadband transfer of RE³⁺ ions between the Stark manifold might be explained by this idea. Alternatively, the absorption cross-section might be calculated using (Martin and Quimby, 2006; Rajaramakrishna *et al.*, 2019).

$$\sigma_{ab} = 2.303 \log \left(\frac{I_o(\lambda)}{I(\lambda)} \right) / NL \quad (1)$$

by which $\log \left(\frac{I_o(\lambda)}{I(\lambda)} \right)$ is the absorbance, N is the Er³⁺ ion concentration (ions/cm³), L is the glass sample thickness.

The emission cross-section is computed using the correlation and the McCumber theory

$$\sigma_{em} = \sigma_{ab} \exp \left[\frac{\varepsilon - h\nu}{kT} \right] \quad (2)$$

by which h is the Planck's constant, k is the Boltzmann's constant, and ν is frequency of emission band, and ε is the temperature-dependent excitation energy. The physical meaning of ε is the net free energy used to excite one Er³⁺ ions from the ⁴I_{15/2} to the ⁴I_{13/2} state at temperature T .

Energy is transmitted from excited to unexcited erbium ions via a resonance mechanism, as seen by the spectrum overlap between the absorption and emission cross-sections. The NIR emission spectra show that the unexcited Er^{3+} ions in the ground state migrate to the excited state and re-emit the absorbed photons due to spectrum broadening in the emitted cross-sectional spectra. They do this by absorbing the photons generated by the excited Er^{3+} ion. The stimulated emission cross-section of Er^{3+} doped glass produced may therefore cover most of the transmission bands used extensively in telecommunications, depending on the excitation level, and operate as a 3-level laser.

For Er^{3+} doped glasses, the absorption data and equations (1) and (2) are used to determine the σ_{ab} and σ_{em} of $^4I_{15/2} \leftrightarrow ^4I_{13/2}$ transitions as a specific wavelength, which are shown in Figures 9(a) - 9(c). The McCumber theory-derived cross-sections for the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of the glasses and other reported glasses are included in Table 1, and the greater σ_{em} results in a low threshold and high gain for laser performance (Thongyoy *et al.*, 2023). Thus, applications utilizing near-infrared lasers may benefit from the novel glass.

Table 1. McCumber theory-derived cross-sections for the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition

Glasses	$\sigma_{ab} \times 10^{-21} \text{cm}^2$	$\sigma_{em} \times 10^{-21} \text{cm}^2$
BGEr0.5 [PW]	1.21	1.60
BGEr1.0 [PW]	1.93	2.52
BGEr2.0 [PW]	9.16	10.80
BiPEr1.0 [Damodaraiah <i>et al.</i> , 2018]	8.54	8.98
MBSEr10 [Jose <i>et al.</i> , 2021]	16.60	16.70
LBBTE1 [Madhu and Srinatha, 2020]	4.64	5.57
LBBPE05 [Madhu <i>et al.</i> , 2018]	5.92	6.78
SBNCEr05 [Rajesh <i>et al.</i> , 2020]	11.64	13.60

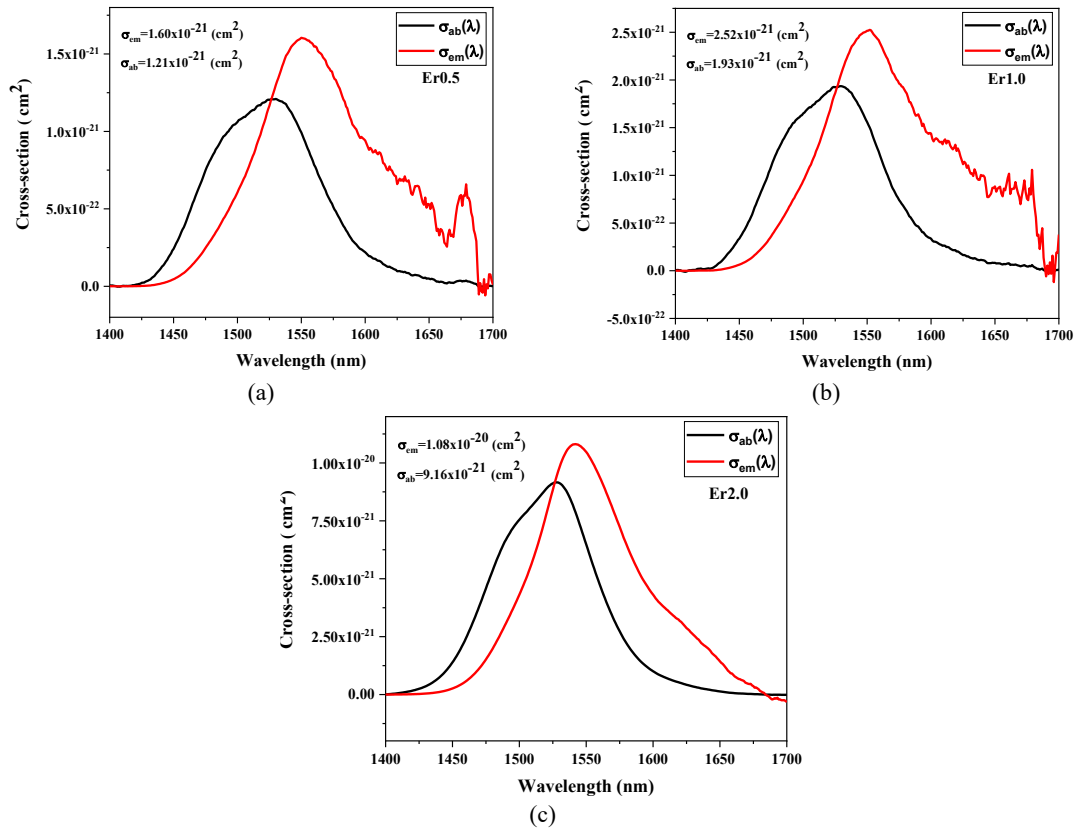


Figure 9. The absorption and emission cross-section of BG glass doped with Er^{3+} is in the NIR region, which (a) Er0.5mol%, (b) Er1.0mol%, and (c) Er2.0mol%

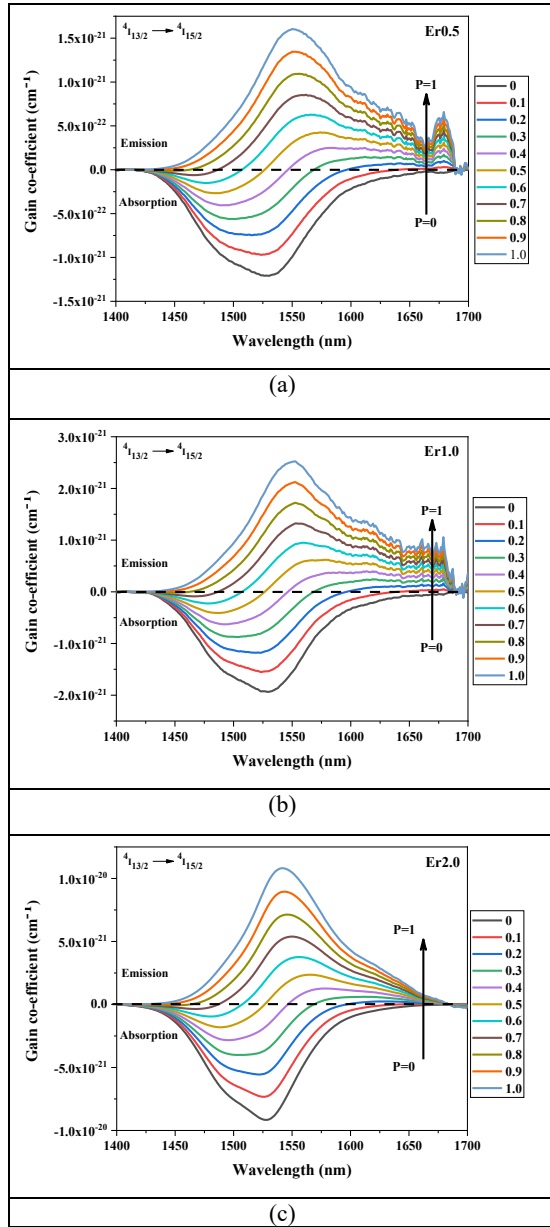


Figure 10. The gain coefficient for $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er³⁺ doped BG glasses, which (a) Er0.5mol%, (b) Er1.0mol%, and (c) Er2.0mol%

Gain cross-section spectra

The optical gain coefficient $G(\lambda)$ is another important factor to consider when evaluating a lasing medium's efficacy since it helps estimate the laser's likely operating wavelength for the optical system (Mariyappan *et al.*, 2019). The $G(\lambda)$ may be calculated using σ_{ab} and σ_{em} values as shown below (Rajaramakrishna *et al.*, 2019):

$$G(\lambda) = P\sigma_{em}(\lambda) - (1 - P)\sigma_{ab}(\lambda) \quad (3)$$

where P is the population inversion rate of $^4I_{13/2}$ to $^4I_{15/2}$ laser transition. Fig.10 presents the gain coefficient $G(\lambda)$, where P has the following values: 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0. Figure 10(a) the BGER0.5 glass shows flat gain in the 1420-1664 nm range for population inversion greater than 0.3, Figure 10(b) the BGER1.0 glass shows flat gain in the 1423-1684 nm range for population inversion greater than 0.3, and Figure 10(c) the BGER2.0 glass shows flat gain in the 1410-1685 nm range for population inversion greater than 0.4. This suggests that for a typical population inversion of more than 40% for BGER2.0 glass system, it might be acceptable for broadband amplifiers used in C-band communication (Rajesh *et al.*, 2020). The wavelength division multiplex (WDM) and optical communications S-band, C-band, and L-band sectors are represented by the experiment's flat gain bandwidth, which ranges from 1410 to 1685 nm (Mariyappan *et al.*, 2019). These bands are defined by fiber to provide WDM, faster speeds, and longer distances. They are a section of the optical spectrum set aside for optical fiber communications (Chen *et al.*, 2003).

Conclusions

The Er³⁺ doped gadolinium yttrium aluminium gallium borate glass was successfully characterized. The addition of Er₂O₃ content in BGER glass results in the density and molar volume increase with increasing Er₂O₃ content in the BGER glass. The refractive index increases with the adding Er₂O₃ content in the BGER glass from 0.05 to 2 mol% due to density increase. In the part of optical properties, the excitation spectra found the higher peak at 1528 nm. The emission spectra found emission of Er³⁺ at 1533 and 1558 by excitation at 523 and 980 nm respectively.

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