The Physical and Optical Studies of Erbium Doped Borosilicate Glass

Nur Ain Nabilah Razali\textsuperscript{1,2}, Iskandar Shahrim Mustafa\textsuperscript{1,2,3}, Nurul Zahirah Noor Azman\textsuperscript{1,2}, Halimah Mohamed Kamari\textsuperscript{3}, Amalina Abd Rahman\textsuperscript{1}, Khairiah Rosli\textsuperscript{1}, Noor Syamimi Taib\textsuperscript{1}, Nur Adilah Tajuddin\textsuperscript{1}

\textsuperscript{1}School of Physics, Universiti Sains Malaysia Main Campus, 11800 USM, Penang, Malaysia.
\textsuperscript{2}Institute of Nano-optoelectronic, Universiti Sains Malaysia, Bukit Jambul, 11900 Bayan Lepas, Penang, Malaysia.
\textsuperscript{3}Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia.

\textsuperscript{a}nurainnabilah_razali@yahoo.com, \textsuperscript{b}iskandarshah@usm.my

\textbf{Abstract.} A glass series of erbium doped zinc borosilicate glass system was prepared by using the melt-quenching method. The absorption spectra revealed several bands at visible range which correspond to the following transitions (from the ground state); \( ^4F_{5/2} + ^4F_{7/2} + ^2H_{11/2} + ^4S_{3/2} + ^4F_{9/2} + ^4I_{9/2} \). The density and molar volume obtained increased and decreased respectively as the concentration of erbium oxide varied from 0 mol \% to 1.0 mol \%. Meanwhile, oxygen packing density (OPD) increased as the concentration of erbium oxide increased up to 3.0 mol \% due to the build-up of bridging oxygen. The indirect band gap energy was achieved from 2.56 eV to 2.80 eV and the Urbach energy values lies between 0.15 eV and 0.61 eV.

1. Introduction

Borosilicate glass is a glass which the main components are silicon dioxide and boron oxide. Borosilicate glass has been produced in a wide range of compositions. The batch materials can be divided into three categories based on their role in the process: glass former, glass intermediate and glass modifier. The most important of any glass batch is always the glass former. Each glass has one or more components which act as the primary source of the structure. These components are commonly designated as glass formers and also called as network formers. These components are the basis for the generic name used for the glass. In this project, both boron oxide and silicon dioxide (SiO\textsubscript{2}) act as network former and namely the glass samples are known as borosilicate glasses \[1\]. Zinc oxide operates as a stabilizer substance in the glass network of ternary and quaternary glass. With the addition of zinc oxide, it will raise the surface tension of the molten and recover the crystallization stability within the substance of the existing section. The rare-earth elements act as glass intermediate. The rare-earth elements (REE) consist of La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb. The rare earths (RE) are highly valued for their unique properties especially as optically active elements in their ionized state for lasers. When incorporated in crystalline or amorphous hosts, the rare earths exist as ion$^{3+}$ \[2\]. The main objectives of the present study are to identify the effect of erbium concentration on physical and linear optical properties of borosilicate glass system, and to explore the possibility the use of Er$^{3+}$ doped
borosilicate glass towards nano-optoelectronic devices. The schematic study on the physical density and absorption erbium doped borosilicate glass had been done. The nonlinear refractive index was analyzed to determine the possibility of the glass materials for nano-optoelectronic field.

2. Materials and Method
2.1 Sample Preparation
Melt quenching technique was used to produce multi-composition glass samples \[(x \% \text{Er}_2\text{O}_3) - (50 - x \% \text{ZnO}) - (20 \% \text{B}_2\text{O}_3) - (30 \% \text{SiO}_2)\] where \(x= 0, 0.5, 1.0, 2.0, 3.0\) and \(4.0\) mol %. The high purity of chemical powder (99.9% purity grade) of erbium (III) oxide, \(\text{Er}_2\text{O}_3\) (REacton, Alfa Aesar), zinc oxide, \(\text{ZnO}\) (Assay, Alfa Aesar) and boron oxide, \(\text{B}_2\text{O}_3\) (Assay, Alfa Aesar) were used for sample preparation. The network former silicon dioxide \(\text{SiO}_2\) 99.37 %, which was obtained from rice husk ash (RHA) is used during the glass fabrication [3]. The raw materials raw materials (7 g) were thoroughly mixed in an alumina crucible and melted at 1300 °C for 2 h in an electric furnace. The melts were quenched on a 250 °C preheated stainless steel mould at in an electric furnace. The stainless-steel mould was left to cool down towards the room temperature. The obtained samples were then polished carefully in order to achieve parallel surface for physical and optical properties measurement.

2.2 Physical Properties Measurement
The density of the glass sample was measured based on Archimedes principle by using distilled water as immersion liquid. Density, molar volume and oxygen packing density were calculated by using equation 1, 2 and 3, respectively.

\[
\rho_s = \rho_{dw} \left( \frac{w_{air}}{w_{air} - w_{dw}} \right)
\]

Where \(M=\)Molecular weight, \(\rho=\)density and \(n=\)number of oxygen atoms per each composition [4].

\[V_m = \frac{M}{\rho}\]  
Oxygen packing density \(= (1000 \times \rho \times n)/M\)

2.3 Optical Properties Measurement
UV-Visible 1800 Shimadzu Spectrophotometer was used to perform optical absorbance measurement of glass structure at room temperature. The spectrometer was set up at absorption mode. The range of wavelength used was between 200 nm to 1000 nm and the absorbance range was from 0 A to 4 A.

3. Results and Discussions
3.1 Physical Properties
The range of thickness for the glass samples is between 4.51 mm to 5.55 mm. The variation of density, molar volume and oxygen packing density (OPD) values as function of \(\text{Er}_2\text{O}_3\) contents are listed in Table 1. The density is found to be increased from 3.46g/cm³ to 3.95 g/cm³ with the increment percentage mole of \(\text{Er}_2\text{O}_3\). The density depends on the multi-composition of the glass network. Eventually, higher structure compactness will produce higher density of the glass. The increment in density indicates that the number of oxygen packing density (OPD) in the glass network increase and decrease in non-bridging oxygen. The increment in molar volume is due to the augmentation in the structure bonding length or the increment in inter-atomic spacing between atoms [5].

3.2 Optical Properties
The absorption spectra of the prepared glass samples consist of 7 fundamental absorption edge, which located at 409, 452, 490, 527, 656, 808 and 980 nm wavelengths as shown in Figure 1. The absorption spectra consist of 7 transitions originating from the ground state \(^4\text{I}_{15/2}\) to the excited states \(^4\text{F}_{5/2} + ^4\text{F}_{7/2} +\)
\(^4\text{H}_{11/2} + ^4\text{S}_{3/2} + ^4\text{F}_{9/2} + ^4\text{I}_{9/2}\). The fundamental absorption edges of the spectra were slightly shifted towards the higher wavelength with the addition of erbium oxide. The shifted of the absorption edge were attributed to structural rearrangements of the glass [6].

![Figure 1: The absorbance of [(x % Er\(_2\)O\(_3\)) - (50 - x % ZnO) - (20 % B\(_2\)O\(_3\)) - (30 % SiO\(_2\))] glass structure.](image)

The absorption coefficient \(\alpha(\omega)\) can be shown as a function of photon energy (for the direct and indirect band gap energy):

\[
\alpha(\omega) = B \frac{(\hbar \omega - E_{\text{opt}})^n}{\hbar \omega}
\]

Where \(n\) is the index number, \(B\) is constant, \(E_{\text{opt}}\) is optical band gap energy and \(\hbar \omega\) is incident photon energy [7]. The Tauc’s plot can be strained between \((\alpha \hbar \omega)^{1/n}\) and \((\hbar \omega)\) by substituting \(n = \frac{1}{2}\) for direct and \(n = 2\) for indirect as illustrated in Figure 2. Whereas, the Urbach energy was calculated using the gradient obtained from Figure 3 based on the given expression:

\[
\alpha(\omega) = B \exp \left( \frac{\hbar \omega}{\Delta E} \right)
\]
The increment of indirect band gap energy due to the decrement in non-bridging oxygen (NBO) is illustrated in Table 1. Higher Urbach energy indicates greater tendency to convert weak bonds into defects [8].
Table 1: Physical properties and Indirect band gap energy, Urbach energy, refractive index, molar refraction and polarizability of \([x \% \text{Er}_2\text{O}_3] - (50 - x \% \text{ZnO}) - (20 \% \text{B}_2\text{O}_3) - (30 \% \text{SiO}_2)\) glass structure

| Mole percentage of \(\text{Er}_2\text{O}_3\) (%) | Indirect band gap energy (eV) | Urbach energy (eV) | Refractive index, \(n\) | Molar refraction, \(R_m\) (cm\(^3\)) | Polarizability, \(\alpha_m\) (10\(^{-24}\)) | Density (g/cm\(^3\)) | Molar Volume (cm\(^3\)) | OPD (g-atom/l) |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 0              | 2.56           | 0.22           | 2.53           | 7.09           | 2.81           | 3.46 ±0.005   | 21.00          | 80.97          |
| 0.5            | 2.72           | 0.61           | 2.48           | 6.87           | 2.72           | 3.57 ±0.008   | 20.80          | 82.23          |
| 1.0            | 2.74           | 0.21           | 2.47           | 6.77           | 2.68           | 3.67 ±0.017   | 20.59          | 83.52          |
| 2.0            | 2.56           | 0.23           | 2.53           | 7.03           | 2.79           | 3.78 ±0.003   | 20.82          | 83.57          |
| 3.0            | 2.76           | 0.17           | 2.46           | 6.87           | 2.72           | 3.89 ±0.009   | 20.99          | 83.85          |
| 4.0            | 2.80           | 0.35           | 2.45           | 6.89           | 2.76           | 3.95 ±0.016   | 21.44          | 83.03          |

Refractive index parameter depends on density and polarizability of the glass materials [9]. Refractive index values were calculated by using the following equation.

\[
\frac{n^2 - 1}{n^2 + 2} = 1 - \frac{E_{\text{opt}}}{\sqrt{20}}
\]  
(6)

Where \(n\) = refractive index, \(E_{\text{opt}}\) = optical band gap energy [10].

The increment in refractive index at 2.0 mol % is because of the addition rare earth ions to the network which leads to the formation of dense packing of rare earth modifiers into the host materials. The higher amounts of dense packing network signify the higher value of refractive index of the glass. The electronic polarizability, \(\alpha_m\) is proportional to the molar refraction, by introducing the Avogadro’s number through the following equation:

\[
R_m = \frac{(4\pi\alpha_m N_A)}{3}
\]  
(7)

\[
R_m = \frac{n-1}{n+2} V_m
\]  
(8)

Where \(R_m\) = molar refraction, \(V_m\) = molar volume. This relationship gives the average value for molar refraction for isotropic substance such as glass [11]. The polarizability decreased with an increased concentration of erbium oxide as illustrated in Table 1. The increment in polarizability at 2.0 mol % and 4.0 mol % are because of high polarity possession which tends to form NBO. Each of \(\text{Er}^{3+}\) will break the bridging oxygen (BO) and lead to formation of NBO atoms. Nevertheless, the lower formation of NBO in the glass network, the lower polarizability of the glass obtained.

4. Conclusion

The melt-quenching method has been used to fabricate erbium doped zinc borosilicate glass system. Several absorption bands are observed in UV–vis absorption spectra for all the glass samples. The absorption bands of erbium and erbium nanoparticles doped zinc borotellurite glasses are located at 409, 452, 490, 527, 656, 808, and 980 nm of wavelengths. The observed absorption bands are due to the 4f–4f transition in erbium and zinc ions in the glass network. The obtained values of physical and linear
optical properties of erbium doped zinc borosilicate glass system may contribute towards the development of solid state devices, optical displays and optical memory devices.

Acknowledgment
The author acknowledges Universiti Sains Malaysia for the financial support for this research under two USM (Short Term Grant) which are 304 / PFIZIK / 6313152 and 304 / PFIZIK / 6313249. Other financial supports grant is from postgraduate USM that is 308/ AIFIZIK/415403.

References
[1] Shelby J.E. 2005 Introduction to Glass Science and Technology. 2nd ed. The Royal Chemistry.
[2] Walsh B.M. 2006 Advances in Spectroscopy for Lasers and Sensing. Springer.
[3] Mustafa I.S, Razali N.A.N, Ibrahim A.R and Kamari H.M 2015 From Rice Husk to Transparent Radiation Protection Material, Jurnal Intelek, 9, pp. 1–6.
[4] Althaf M., and Chaudhr A.M 2010 Physical Properties of Lithium Containing Cadmium Phosphate Glasses. Journal Modern Physics, 1, pp.201-05.
[5] Halimah M.K, Daud W., Sidek H., Zaidan H., and Zainal A. 2010 Optical properties of ternary tellurite glasses. Materials Science-Poland 28(1), pp. 173-180.
[6] Said Mahraz Z.A, Sahar M.R, and Ghoshal S.K, 2014 Band gap and polarizability of boro-tellurite glass: Influence of erbium ions. Journal of Molecular Structure, 1072(1), pp. 238–241.
[7] Sushama D. and Predeep P. 2014 Thermal and Optical Studies of Rare Earth Doped Tungston-Tellurite Glass. International Journal of Applied Physics and Mathematics, 4(2), pp.139-43.
[8] Ashur Z., Mahraz S., Sahar M.R, Ghoshal S.K, and Dousti M.R 2013 Concentration dependent luminescence quenching of Er3+-doped zinc. Journal of Luminescence, 144, pp. 139–145.
[9] Azlan M.N, Halimah M.K, Siti S.Z and Daud W.M 2013 Effect of Erbium Nanoparticles on Optical Properties of Zinc Borotellurite Glass System. Journal of Nanomaterials, pp.168.
[10] Said Mahraz Z.A, Sahar M.R, Ghoshal S.K, and Reza Dousti M., M 2013 Concentration Dependent Luminescence Quenching of Er3+- Doped Zinc Boro Tellurite Glass. Journal of Luminescence, 144, pp.139-45.
[11] Dimitrov V. and T. Komatsu 1999 Electronic Polarizability, Optical Basicity and Non-Linear Optical Properties of Oxide Glasses. Journal of Non Crystalline Solids, 249, pp.160-79.