Tuning Optical and Structural Properties of Composite Glass: Effect of Rice Husk Fibre

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Abstract. Tuning optical and structural properties of composite glass due to the effect of rice husk fibre are examined. A series of glass with composition of $69.5\text{TeO}_2 - 20\text{ZnO} - 10\text{Na}_2\text{O} - 0.5\text{Er}_2\text{O}_3 - (x)0.2\text{RHF}$ where $x$ is rice husk fibre in weight percentage with three distinctive sizes of 63 $\mu$m, 125 $\mu$m and 250 $\mu$m are prepared following melt-quenching technique and characterized systematically. UV-Vis spectra displayed nine absorption bands centered at 380, 410, 445, 489, 520, 545, 650, 799 and 975 nm corresponding to the transitions of $\text{Er}^{3+}$ originate from ground state to excited states. The direct and indirect band gap is found to lies in range of 3.296 to 3.410 eV and 2.958 to 3.174 eV, respectively. Urbach energy lies in the range of 0.145 to 0.181 eV. SEM images illustrates the fractures surface due to porosity of glass samples and elemental traces verify the appearance of C, O, Na, Zn, Te, Au, Al, Si, Er and Ca elements.

Key words: Composite, fibre, glass, non-bridging oxygen, rice husk

1. Introduction

Organic wastes are beneficial in terms of energy, water content and mineral content. However, current methods of waste disposal do not utilize these resources [1]. Therefore, the main emphasis of materials science in sustainable civil engineering world is enhancing the performance and functionality of conventional materials in environmentally friendly way using recent technologies and local waste materials [2]. Rice husk is an agriculture residue either it is burned or dumped as waste [3]. Generally, about 20 to 25 wt% of rice husk ash containing more than 90% silica with traces of other metal oxides is formed during burning process [4].

Tellurite based glass exhibits a beneficial quality of glass forming ability, wide transmission band, fast optical switches, excellent linear and nonlinear optical properties, and exceptional optical fibres for fibre-optical communications. Tellurite based glass is widely being used as the main host materials to achieve excellent optical and dielectric properties due to their valuable features [5]. According to Tuscharoen and co-workers [6], the optical and shielding properties of $\text{BaO}:\text{B}_2\text{O}_3$: RHA (rice husk ash) is better than the commercial window and ordinary concrete. Meanwhile, Kaewkhao and Limsuwan [7] reported that color reflects a significant property of a glass object in the glass science. They demonstrated the replacement of silica prepared from rice husk to fabricate the color glass [7]. In present work, the rice husk fibre (RHF) with varying sizes is incorporated into the glass matrix. Accordingly, the data on optical and structural properties of composite glass are examined thoroughly.
2. Materials and Methods

2.1 Extraction of Rice Husk

The extraction of rice husk is based on previous research demonstrated by Low and Lee [8]. The first step involved the winnowing process of rice husk to remove the stones, sand, and dust. Figure 1 shows the unprocessed rice husk.

![Unprocessed rice husk](image)

Figure 1. Unprocessed rice husk

Then, the RHF are washed thoroughly by using distilled water and subjected to drying process under the sunlight. The second step required 20g of RHF treated with 1% of Na$_2$CO$_3$ solution. The mixture is shaken for 45 minutes at room temperature. Then, the rice husk is rinsed by using distilled water for several times and dried under the sunlight. The dried RHF then are blended to achieve a fine powder. Lastly, the RHF are subjected to a sieving process to separate the fine powder into the distinctive sizes of 63 µm, 125 µm and 250 µm as shown in Figure 2. A distinctive size of RHF in the range of 63 µm, 125 µm and 250 µm are obtained by using sieving machine with model of RX-29 (Tyler USA).

![Distinctive sizes of RHF after sieving process](image)

Figure 2. Distinctive sizes of RHF after sieving process shows fibre with (a) 63 µm, (b) 125µm and (c) 250 µm

2.2 Fabrication and Characterization of Glass

The glass composition of 69.5TeO$_2$–20ZnO–10Na$_2$O–0.5Er$_2$O$_3$–(x)0.2RHF are synthesized by using melt-quenching technique, where x represent the rice husk fibre in weight percentage with three distinctive sizes of 63 µm, 125 µm and 250 µm as summarized in Table 1. The specific weight of TeO$_2$, ZnO, Na$_2$O, Er$_2$O$_3$ and RHF are mixed thoroughly. The batches are subjected to a milling process for 30 minutes to get homogeneous mixture.

A platinum crucible containing the glass constituents is placed in a furnace with temperature at 950 °C for 15 minutes. Then, the molten is poured in a brass and is kept at room temperature for 48 hours. Finally, the samples are ready for optical and surface morphology measurements. The absorbance spectra are recorded by using CARY-60 UV-Visible light spectroscopy in range of 353 – 1100 nm. SEM-EDX analysis is carried out by using Hitachi 3400N VP-SEM for elemental traces. All measurements are carried out under room temperature. The thickness of glass samples is determined
by using vernier caliper with a model of Tesa Shop Cal 6”/150 mm with resolution of 0.01mm/0.0005”.

| Glass code      | Glass composition                      |
|-----------------|----------------------------------------|
| TZNE            | 69.5 TeO₂ – 20 ZnO – 10 Na₂O – 0.5 Er₂O₃ |
| TZRERHF63       | 69.5 TeO₂ – 20 ZnO – 10 Na₂O -0.5 Er₂O₃– 0.01g 63µm RHF |
| TZRERHF125      | 69.5 TeO₂ – 20 ZnO – 10 Na₂O -0.5 Er₂O₃ – 0.01g 125µm RHF |
| TZRERHF250      | 69.5 TeO₂ – 20 ZnO – 10 Na₂O -0.5 Er₂O₃ – 0.01g 250µm RHF |

3. Results and Discussion

3.1 Optical Characterization

Optical absorption in solids occurs due to the coupling of the electric field of the incident radiation to the dipole moment in the material and the consequent transfer of energy. In addition, the absorption edge in oxide glasses corresponds to the transition of an electron belonging to an oxygen ion to an excited state [9].

The room temperature UV-Vis absorption spectra of Er₂O₃ doped glasses as shown in Figure 3 is comprised of nine absorption bands centered at 380, 410, 445, 520, 545, 650, 799 and 975 nm that originate from the ground state ⁴I₁₅/₂ of Er³⁺ ions to ⁴G₁₁/₂, ⁴F₁₀/₂, ⁴F₅/₂, ⁴F₇/₂, ²H₁₁/₂, ²S₃/₂, ²F₉/₂, ⁴I₉/₂ and ⁴I₁₁/₂ excited states transitions, respectively. In current work, the determination of transition energy from ground state to excited state of Er³⁺ ions following the previous work demonstrated by Carnall and co-workers [10].

![Absorption Spectra](image)

Figure 3. UV-Vis absorption spectra of glass samples in range of 353 – 1100 nm
The expression for \( \alpha(\omega) \) as a function of photon energy for optical band gap can be expressed as

\[
\alpha(\omega) = \frac{B(h\omega-E_{opt})^{n_B}}{h\omega}, \tag{1}
\]

where \( B \) is a constant called the band tailing parameter, \( E_{opt} \) is the optical band gap and \( h\omega \) is the photon energy and \( n_B \) is an index which is \( \frac{1}{2} \) for direct and \( 2 \) for indirect transitions [11]. The band gaps for both the inter-band transitions are obtained from the above relations. The direct band gap does not involve the phonon mediated interaction [12], whereas the indirect transitions involve simultaneous interaction with lattice vibrations and the wave vector of the electron [13]. The indirect transitions are valid according to the Tauc relations with \( n_B = 2 \) for amorphous materials. The values of indirect optical band gap energy can be obtained by extrapolating the absorption coefficient to zero in the \((a\hbar\omega)^{1/2}\) versus \( \hbar\omega \) plot [14]. Figure 4(a) and 4(b) shows the Tauc plot for indirect and indirect band gap measurement.

Urbach edge is an exponential increase of the absorption coefficient with photon energy illustrates the main feature of the absorption edge of amorphous materials. The increase in absorption coefficient is followed with an exponential decay of density of states localized into the gap when the energy of the incident photon is less than the band gap. The lack of crystalline long-range order in amorphous or glassy materials is associated with a tailing of density of states into forbidden energy. The band tail associated with valence band and conduction band is developed due to the random potential fluctuations in material which extends into the energy gap manifesting an exponential behavior [8]. The extent of this tailing is a measure of the disorder in the material and can be estimated using the Urbach equation given by

\[
\alpha(\omega) = B \exp\left(\frac{\hbar\omega}{E_{tail}}\right), \tag{2}
\]

where \( E_{tail} \) is Urbach energy corresponds to the optical transitions between localized tail states adjacent to the valence band and the extended states in the conduction band which occurs above the mobility edge [13]. The values of \( E_{tail} \) are calculated from the reciprocal of the slope of the linear region of \( \ln(\alpha) \) versus \( \hbar\omega \) plot [11]. Figure 4(c) shows the \( \ln(\alpha) \) against photon energy \( \hbar\omega \) for Urbach energy measurement.
Table 2 summarizes the thickness, direct band gap ($E_{\text{dir}}$), indirect band gap ($E_{\text{indir}}$) and Urbach energy ($E_{U}$) for all glass samples. The direct band gap and indirect band gap are found in range of 3.296 – 3.410 eV and 2.958 – 3.174 eV, respectively. The Urbach energy of all glass samples are lies in range of 0.145 – 0.181 eV. Figure 5(a) and 5(b) shows the variations in direct band gap, indirect band gap and Urbach energy of glass samples with varying sizes of RHF incorporated into the glass matrix.

The incorporation of RHF with size of 63 μm cause small decrement in direct and indirect bad gap due to glass structure become progressively crowded with Ca$^{2+}$ ions [9]. However, further addition of RHF with bigger sizes of 125 μm and 250 μm led to the increment in direct and indirect band gap due to substitution of Ca atoms from RHF [3] in glass structure and create open network with non-bridging oxygen (NBO) [9, 15]. In current work, the optical band gap of all samples is found to be lower than the pure TeO$_2$ with a value of 3.79 eV [16]. Disorder in the material illustrates by the existence of a band tailing in the forbidden energy band gap in glass and amorphous materials [11]. The decrease in Urbach energy from 0.181 to 0.145 eV with incorporation of bigger size of RHF signifies the decreasing degree of disorder in the glass samples [11].
Table 2. Thickness, direct band gap, indirect band gap and Urbach energy for all glass samples

| Glass code   | Thickness (mm) | Direct band gap (E_{dir}, eV) | Indirect band gap (E_{indir}, eV) | Urbach energy (E_{U}, eV) |
|--------------|----------------|-------------------------------|-----------------------------------|---------------------------|
| TZNE         | 3.80           | 3.342                         | 3.059                             | 0.181                     |
| TZNERHF63    | 3.68           | 3.296                         | 2.958                             | 0.173                     |
| TZNERHF125   | 3.68           | 3.301                         | 3.018                             | 0.159                     |
| TZNERHF250   | 3.67           | 3.410                         | 3.174                             | 0.145                     |

Figure 5. Variation in (a) direct and indirect band gap (b) Urbach energy with different sizes of RHF

3.2 Surface Morphology

Figure 6(a) shows SEM image of glass sample without RHF content. Meanwhile, Figure 6(b)–6(d) shows glass samples with RHF content with varying sizes of 63 µm, 125 µm and 250 µm. It can be observed that the surface morphology of glass sample without RHF content shows much appearance of fractured surfaces of the glass indicate more porosity [17]. Backscattered electrons in SEM facilitates the generation of an image in the microscope that shows the different elements present in a sample. Backscattered electrons emission intensity is a function of the material’s atomic number. From SEM images as in Figure 6, atoms with higher atomic number appear brighter than those with lower one [18]. Backscattered signal is found to be higher due to the elements with higher atomic numbers have more positive charges on the nucleus and cause more electrons are backscattered [19].
Figure 6. SEM images of (a) TZNE glass, (b) TZNERHF63 glass, (c) TZNERHF125 glass and (d) TZNERHF250 glass

The typical EDX spectrum of TZNERHF125 glass sample from selected area as shown in Figure 7 exhibits C, O, Na, Zn, Te, Au, Al, Si, Er and the Ca peak which is attributed to the elemental traces in the glass matrix surrounding. Table 3 shows the elements with their respective weight% and atomic%. K, L and M represent the inner shell electrons as shown in Table 3. The presence of detected elements confirms the successful preparation of the desired glass samples. The intense peak located at 0.5 keV is connected with the domination of oxygen (O) in the sample. The coating material based vacuum-evaporated gold cause the appearance of gold (Au) peak. Glass samples are electrically non-conducting. Hence, a path for the incident electrons to flow to ground a conducting surface coating must be applied. To produce the spectrum, the EDX analyses taking account for the accelerating voltage of the beam. Then, the calculations process will take over to create sensitivity factors that will convert the area under the peak into weight or atomic percent [20].

Figure 7. EDX spectra of TZNERHF125 glass
Table 3. Elemental trace from EDX for TZNERHF125 glass

| Element      | Series | Experimental (Weight%) | Experimental (Atomic%) |
|--------------|--------|------------------------|------------------------|
| Carbon (C)   | K-series | 0.52                   | 2.85                   |
| Oxygen (O)   | K-series | 9.87                   | 40.71                  |
| Sodium (Na)  | K-series | 2.15                   | 6.16                   |
| Zinc (Zn)    | K-series | 11.26                  | 11.36                  |
| Tellurium (Te)| L-series | 57.53                  | 29.74                  |
| Gold (Au)    | M-series | 14.11                  | 4.72                   |
| Aluminium (Al)| K-series | 0.04                   | 0.09                   |
| Silicon (Si) | K-series | 0.05                   | 0.13                   |
| Erbium (Er)  | L-series | 2.50                   | 0.98                   |
| Calcium (Ca) | K-series | 1.97                   | 3.25                   |

4. Conclusion

Erbium-doped zinc sodium tellurite glass with and without RHF content are prepared using melt quenching method. The effect of varying sizes of RHF is investigated. Variations in direct and indirect band gap ranging from 3.296 eV to 3.410 eV and 2.958 eV to 3.174 eV due to the generation of NBO. The optical band gap which exhibits by all glass samples may be potential candidates for optoelectronics devices. The decrement in Urbach energy from 0.181 eV to 0.145 eV is due to decreasing degree of disorder with incorporation of bigger RHF. SEM images signify the surface morphology of glass samples and EDX spectra shows the elemental traces of C, O, Na, Zn, Te, Au, Al, Si, Er and Ca.

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