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Physical, structural and optical properties of erbium doped rice husk silicate borotellurite (Er-doped RHSBT) glasses

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ABSTRACT

A series of erbium doped rice husk silicate borotellurite glasses with chemical composition $\{[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.8}(SiO_2)_{0.2}\}_{1-x}(Er_2O_3)_x$ with x = 0.01, 0.02, 0.03, 0.04 and 0.05 mol was prepared using the melt-quenching technique. The density and the molar volume were determined and found to be increasing with Er^{3+} concentration. The glasses were subjected to FTIR and XRD to study the structural changes in the glass. UV–Vis spectroscopy was carried out to obtain the absorption spectrum that is used in the calculation of the optical energy band gap (Direct and Indirect), the Urbach energy and the refractive index. Using the refractive index, density and molar volume, the molar polarizability, metallization criterion, polaron radius, average boron-boron separation, inter-nuclear distance of Er^{3+}, surface reflection loss, transmission coefficient and oxygen packing density were determined. The density, molar volume, optical band gaps, molar refraction, transmission coefficient and metallization criterion were found to have increased with increasing concentration of Er^{3+} ions. While the values of the refractive index, Urbach energy and inter-nuclear distance of Er^{3+} ions decreased. As more Er^{3+} ions were introduced, the reflectivity of the glasses decreased. The polaron radius also decreased, with the values suggesting that the glass has small polaron.

1. Introduction

Tellurite glasses are increasingly studied in the recent years due to their promise in various applications. The glasses are promising in the non-linear optical applications, lasers, sensors, optical fibers and solar cells, with appropriate rare earth (RE) ions doping [1,2].

Tellurium oxide (TeO_2) as a conditional glass former with high refractive index, low melting point and low phonon maxima, needs modifying ions to easily form glass [1]. Boron oxide (B_2O_3) is excellent material for combination with TeO_2 as it improves the glass quality in terms of transparency, RE ions solubility and hardness [2].

Silica (SiO_2) has been used as substrates for electronic displays, optical fibers, optical disc, medical and dental implants and radiation shielding. SiO_2 is mostly used in glasses to give them mechanical quality [3].

Extraction of silicate (silica) from the rice milling waste (rice husk or rice paddy) for commercial and scientific use is one of the alternative solutions to its disposal problems [4]. Different researchers have used different techniques to extract silica from the rice husk with different degrees of purity from 80 to 99% [6–9].

Erbium as an excellent glass doping element is famously used in communication technology for optical signal amplification in the Erbium doped fiber amplifier (EDFA). Many glass scientists have carried out several works on the influence of Er^{3+} ions on the physical, structural, optical, electrical and mechanical properties of different glass compositions [1,10–12].

This work sorts to study the erbium doping effects on some physical, structural and optical properties of rice husk silicate borotellurite glasses. This includes the density, molar volume, optical energy band gap, refractive index, molar refractive index, reflectivity (reflection loss at the glass surface), transmission coefficient, molar polarizability, polaron radius and so on.

The inclusion of the rice husk silicate is important as it provides another waste utilization alternative as well as help in providing a much stronger glass. This will also provide an alternative for a more profitable utilization of the rice waste. The rice husk silicate composition was selected and fixed as 20% molar ratio as it appeared to be the best in terms of transparency and high refractive index.

2. Experimental section

A series of erbium doped silicate borotellurite glasses where

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prepared using the chemical formula $\{[(TeO_2)_{0.7}\ (B_2O_3)_{0.3}]_{0.8}(SiO_2)_{0.2}\}_{1-x}(Er_2O_3)_x$ with x = 0.01, 0.02, 0.03, 0.04 and 0.05 mol by the use of conventional melt-quenching technique. The chemical reagents used are TeO_2 (Alfar Aeser, 99.9%), B_2O_3 (Alfar Aeser, 99.9%), Er_2O_3 (Alfar Aeser, 99.9%) and SiO_2 (Rice Husk extracted, 98.548%).

The silicate used was extracted from the rice husk (waste from rice milling). The husk was first washed three times using normal water and with deionized water the fourth time, to rid it from dust like impurities after the water is drained using a plastic bowl [5]. The drained sample was then leached in hydrochloric acid (HCl, 2 M) for about two hours [6]. The husk was then drained off the acid and washed with deionized water to get the acid off the fabrics of the husk. The husk was then drained of the deionized water for 24 h and dried in an oven at 120 °C for about 4 h. Finally, the dried rice husk was then incinerated at 700 °C for about 6 h to obtain the rice husk ash (silicate) [7].

To prepare the glasses, 12 g of the powdered chemicals were weighed in the molar proportion presented by the above chemical formula using a high precision digital weighing machine (± 0.0001). The weighed chemicals were mixed and stirred for 30 min to ensure homogeneity in the mixture. The homogeneous mixture was then preheated for an hour in a furnace at 400 °C and later transferred to another furnace at temperatures 900 °C for another one to two hours for melting of the sample. For glass casting, the glass was allowed to anneal at 400 °C for 1 h. The prepared glass was cut and then polished using silicon carbide [8].

The densities of the glass samples were measured based on the famous Archimedes principle using an electronic densimeter MD-300S (Alfa Mirage). The equation is given as;

$$\rho_{sample} = \frac{w_{air}}{w_{water}}\rho_{water} \quad (1)$$

The molar volume was obtained for each sample using the equation.

$$V_m = \frac{m_w}{\rho_{sample}} \quad (2)$$

where ρ_{sample}, ρ_{water}, w_{Air}, w_{water} and m_w are the sample density, water density, weight of sample in air, weight of sample in water and molar weight of the glass sample respectively [9].

The optical absorption spectrum for the glass samples were determined using UV–Visible spectrometer Shidamatsu Model UV-1650PC with wavelength range from 200 nm to 800 nm. FTIR spectroscopy was carried out on the powdered portion of the glasses to obtain the structural nature of the glass based on the behavior of its functional groups when the material interacts with infrared waves. This was carried out at the wave number range of 280–4000 cm^{-1}. The XRD spectroscopy was carried out on the powdered portion of the glass samples between $20 < 2\theta < 80$ to determine the crystalline or amorphous nature of the glass.

3. Result and discussion

The structure of the silicate obtained was found to be amorphous from the XRD analysis. As with the hypothesis that the crystalline or amorphous nature of the silica depends on the incineration temperature at which it was extracted on; that at burning temperatures below 700 °C, the rice husk silica obtained was amorphous [7].

4. XRD analysis

The amorphous or crystalline nature of the glass determined from the XRD pattern as shown in Fig. 1 for the Er doped RHBTS glass samples revealed a broad diffused scattering around $2\theta = 20°–30°$. This exhibits the amorphous nature of the glass and shows absence of long range atomic arrangements [16,22].

5. XRF analysis

As shown in Table 1, the silicate obtained has about 98.548% purity. The processes of leaching and washing were carried out at room temperature, unlike the method adapted by Mustafa and co-workers which require the use of heat [5]. The purity of the extracted silicate depends on the method and the conditions of extraction, which includes the leaching temperature, acid concentration and the burning temperature [7,13,15].

6. Density and molar volume

Structural changes in glass network due mostly to changes in cross-link density, coordination number, structural compactness, geometrical configuration, and dimension of interstitial spaces of the glass are the factors that affect the glass density value [8]. Obtained density values can be used in analyzing the physical, structural, optical, thermal and the elastic properties of glass material [11, 16 17].

From Fig. 2, the density of erbium doped rice husk silicate borotellurite (Er doped RHBTS) glass increased with addition of more Er ions in the glass network. The increase in the density may be connected to the substitution of lighter atoms of Te, B and Si with heavier atoms of Er in the network which resulted to increase in the mean molecular weight of the glass [18,19]. Density increase in the glass may also result to a change in the cross-link density in the glass [10].

The molar volume was obtained from the density and molar mass values of the glass. The molar volume as can be seen in Fig. 3 increased when more Er ions were introduced in the glass network. As the FTIR result presented in Fig. 13, the addition of more Er ions in the network led to production of more TeO_3 and TeO_4 units in the network and eventually increasing the number of non-bridging oxygen (NBO) in the network [10]. The increase may also be attributed to the substitution of atoms of smaller atomic/ionic radii (Te, B and Si) with Er atoms with larger atomic/ionic radius [11].

7. Absorption spectrum

Fig. 4 shows the UV–Vis absorption spectra of Er^{3+} doped RHSBT glass samples in the wavelength interval of 400 to 800 nm. The characteristic absorption bands corresponding to the transitions from the ground states to excited states of Er^{3+} are 651, 522,488, 448.5 and 403 nm are attributed to transition from the ground state of $^4I_{15/2}$ to the excited states of $^4F_{9/2}$, $^2H_{1/2}$, $^4F_{7/2}$, $^4F_{3/2}$ and $^2G_{11/2}$ respectively (Fig. 4). The absorption intensity is highest around 521 nm and decreases in the order of 651, 488, 403 and 448.5 nm [2,10,24]. The weak absorption recorded around 534 nm may be due to the overlap of $^4S_{3/2}$ with the upper $^2H_{11/2}$ excited states [12]. The characteristic absorption peaks position may be slightly affected by the medium or the hosting material and the nature of the bonding around the transition element in the study [13].

8. Other optical and structural and physical features

The optical band gap (Direct and Indirect) was determined using the Davis and Mott expression for the absorption coefficient α (υ) as;

$$\alpha(\upsilon) = B\frac{(h\upsilon - E_{opt})^n}{h\upsilon} \quad (3)$$

where E_{opt} is the optical band gap, n is a number, with $n = 2$ for indirect and $n = 1/2$ for direct allowed transitions and B is a constant [10,25]. The value of α (υ) is the absorption coefficient obtained using the expression;

$$\alpha(\upsilon) = 2.303\frac{A}{t} \quad (4)$$

where t is the sample thickness, A is the value of the corresponding