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INFLUENCE OF ERBIUM CONCENTRATION ON SPECTROSCOPIC PROPERTIES OF TELLURITE BASED GLASS

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ABSTRACT

Erbium zinc borotellurite, $\{[(TeO_2)_{0.70}(B_2O_3)_{0.30}]_{0.7}\ (ZnO)_{0.3}\}_{1-y}\ (Er_3O_2)_y$ glasses were prepared by rapid melt-quenching method. The structural properties of the glass samples were determined by using x-ray diffraction (XRD) method and was confirmed its amorphous nature. The FTIR analysis shows that the Erbium Oxide increases the number of non-bridging oxygen that affects the bonding structure of TeO_2, ZnO and B_2O_3. The absorption edge gives the value of band gap E_{opt} and Urbach energy ΔE. The value of E_{opt} lies between 3.025 eV and 3.440 eV for indirect band gap and between 3.500 eV to 3.680 eV in the direct band gap. The Urbach energy shows non-linear with the concentration of Erbium Oxide and varies within 0.153 eV and 0.200 eV.

Keywords: Optical materials; Fourier transform infrared spectroscopy (FTIR); Optical band gap

INTRODUCTION

Extensive research on tellurite based glass has been continuously conducted [1,2,3]. It is well known that tellurite based glass possesses a high potential to enhance the functionality of fibre optics. This is due to their excellent optical and dielectric properties such as a high refractive index, high dielectric constant, good glass forming ability and excellent suitability with rare earth materials.

The recent research on rare earth doped tellurite glass has been extensively discovered due to their potential applications in many areas, especially in optical communication [4,5]. Rare earth doped fiber amplifier is used to enhance the optical communication and one of the applications is Er^{3+}-doped fiber amplifier (EDFA) devices.

Thus, this research has focused on the optical properties of erbium zinc borotellurite glass. The main areas of the optical properties that will be covered are the optical coefficient and band gap. Moreover, density and molar volume of the glass system were also investigated. FTIR and XRD were used to analyze the structural properties of the glass sample.

EXPERIMENTAL TECHNOQUES

The glass samples with the composition of $\{[(TeO_2)_{0.70}(B_2O_3)_{0.30}]_{0.7}(ZnO)_{0.3}\}_{1-y}(Er_3O_2)_y$ y=0.005, 0.01, 0.02, 0.03, 0.04, 0.05 were prepared by using rapid melt-quenching method. The high purity (99.99%) of chemical powder of erbium oxide, tellurium oxide, boron oxide and zinc oxide were weighed by using digital weighing machine and mixed together thoroughly in alumina crucible. The alumina crucible with the mixture of the chemical powder was heated at 400 ^oC in 1 hour by using electrical furnace to remove the excess hydrogen content.

The alumina crucible was then heated at 900 °C in 2 hours for the melting process. The molten obtained after the melting process was quenched in a stainless steel mould that was pre-heated at 400 ^oC. The mould was then annealed at 400 ^oC in 1 hour. The furnace was then turned off to cool down the glass sample at room temperature. The glass sample was cut into a pallet by using Isomet Buehler low speed saw machine. The pellet sample was polished to obtain smooth and clean surface.

The refractive index was measured by using EL X-02C high precision Elipsometer with the angle of incident 70^o and 632.80 nm of light source. The optical absorption was obtained by using UV-1650PC UV-Vis Spectrophotometer (Shimadzu) with wavelength in the range 190-1100 nm.

RESULTS AND DISCUSSION

Fourier Transform Infrared (FTIR)

Infrared spectroscopy is an analysis method that provides structural studies into the interaction between alkali metal and borate glass network [6]. The transmission spectra of the $\{[(TeO_2)_{70}(B_2O_3)_{30}]_{70}(ZnO)_{30}\}_{100-y}(Er_3O_2)_y$ glass system were recorded on various contents of erbium oxide. The spectra are presented in Figure 1. The transmission spectra of the glass system consists of three wide absorption bands between 656 – 664 cm^{-1}, 1233 – 1252 cm^{-1} and 1327 – 1343 cm^{-1}. In addition, some shoulders were recorded at 414 cm^{-1} - 421cm^{-1} and 2000 - 3744 cm^{-1} in the glass system.

The characteristic of pure TeO_2 glass is the absorption band was centered at 640 cm^{-1} [7]. Trigonal pyramid TeO_3 and bipyramid TeO_4 is the reference to determine the structure pattern of tellurium containing glasses. Stretching vibrations of Te-O bonds in TeO_4 and TeO_3 groups are used to determine the absorption band in the range of 600-700 cm^{-1} in tellurium containing glasses. This can be genera1lized that the absorption band in the range of 650-700cm^{-1} correlates with TeO_3 group and the absorption band in the range of 600-650 cm^{-1} correlates with TeO_4 group. The appearance band at 656-664 cm^{-1} is a proved of the TeO_3 group exists in all tellurite containing glass by analyzing the obtained results of the glass system. The present of ZnO introduces the formation of the-O-Zn by breaking up the Te-O-Te bond at low ZnO proportion and the Te-O-B bonds indicates the coordination effects known as dangling bonds (Te-0- .. Zn^{2+}.. O-

Te), that decrease the TeO_3 units by forming TeO_4 units [8]. The appearance of absorption peak at 414 cm^{-1} and 421 cm^{-1} of pure zinc borotellurite glass system with 0% mole erbium indicates that the ZnO participate in the glass network with ZnO_4 structural units and alternate with TeO_4 units. Besides that, this band disappears when introduce Er_2O_3 content into the glass network. This indicates that zinc lattice is completely broken down. The vibration of B-O-B linkage is attributed at absorption peak of 694cm^{-1} and both boron atom are triangular coordinated.

The structure of pure B_2O_3 consists of a random network of boroxyl rings at around 806 cm^{-1} where this band disappears during the formation of glass network which means no boroxyl rings in the glass structure. The BO_3 and BO_4 groups were introduced after the glass formation and these groups were bonded in the formation of the random network. This corresponds to the substitutions of BO_3 and BO_4 into the glass network [7]. The assignment of the IR bands to specific vibrations in borate groups will be based on the work of Krogh-Moe [9]. The transmission spectra of borate glass can be divided into three regions: (1) 600-800 cm^{-1}(bending vibrations of various borate arrangements B-O-B), (2) 800-1200 cm^{-1}(B-O is stretching of tetrahedral BO_4- units), (3) 1200-1800 cm^{-1}(B-O is stretching of trigonal BO_3 units). The band at about 1233-1253 cm^{-1} associated to the B-O (B) stretching vibrations of polymerized BO_3 groups [10]. Band at about 1327 – 1343 cm^{-1} correspond to the trigonal B-O bond stretching vibrations in isolated trigonal BO^3 units. Furthermore, bands at about 1200-1253 cm^{-1} are assigned to the trigonal B-O bond stretching vibrations of BO_3 units from boroxyl groups and 1388 - 1410 cm^{-1} correspond to trigonal B-O bond stretching vibrations of BO_3 units from varied types of borate groups. This is proven by the absorption band obtained in the range of 1233-1253 cm^{-1} and 1327 – 1343 cm^{-1}.

The band between 2100 cm^{-1} and 3742 cm^{-1} indicates the vibration of OH groups. A possible reaction of producing OH group in the glass can be expressed as $H_3BO_3 \rightarrow B_2O_3 + H_2O$, since H_3BO_3 was acted as a starting material in the sample preparation process [10].

Hence, the increase of erbium ion concentrations of the samples makes the absorption peaks become broader and their intensity becomes smaller [11]. This is clearly shown that the addition of erbium oxides composition from 0 to 5 mol % makes the absorption peaks become broader and less intensity. In general, the band shift of these groups depends on the changes in the composition of the glass network.

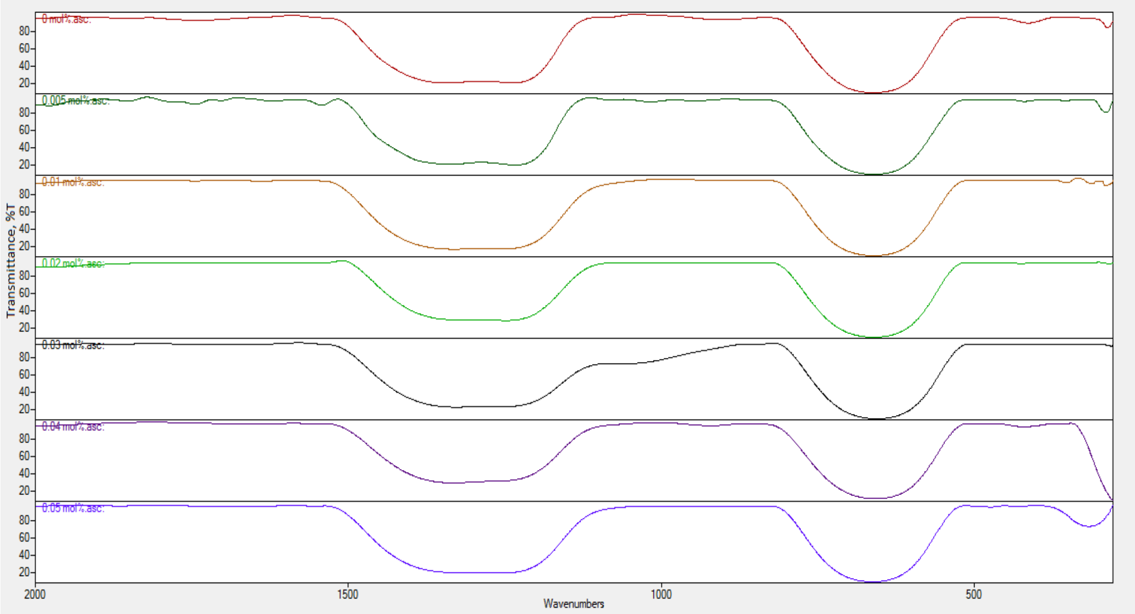

Figure 1 : FTIR spectra of zinc oxide, boron oxide, tellurite oxide, erbium oxide and $\{[(TeO_2)_{70}\ (B_2O_3)_{30}]_{70}\ (ZnO)_{30}\}_{100-y}\ (Er_3O_2)_y$ glass system

X-ray Diffraction (XRD)

Figure 2 shows the XRD patterns for different composition of $\{[\ (TeO_2)_{0.70}\ (B_2O_3)_{0.30}]_{0.7}\ (ZnO)_{0.3}\}_{1-y}\ (Er_3O_2)_y$,where y=0,0.005,0.01,0.02,0.03,0.04 and 0.05 mol%. All the glass samples were found to show no discrete or continuous sharp peaks but broad halo at around $2\Theta=30^0$. It is noted in Figure 2 that there has broad peak at around $2\Theta= 30^0$ or all the glass samples. There are no sharp peaks shown from the result of the glass samples $y<0.05$ mol% which means all the glass samples phase are amorphous. In general, a glass is supposed to be a random arrangement of molecules and below the transformation regions, the molecules are much less mobile.

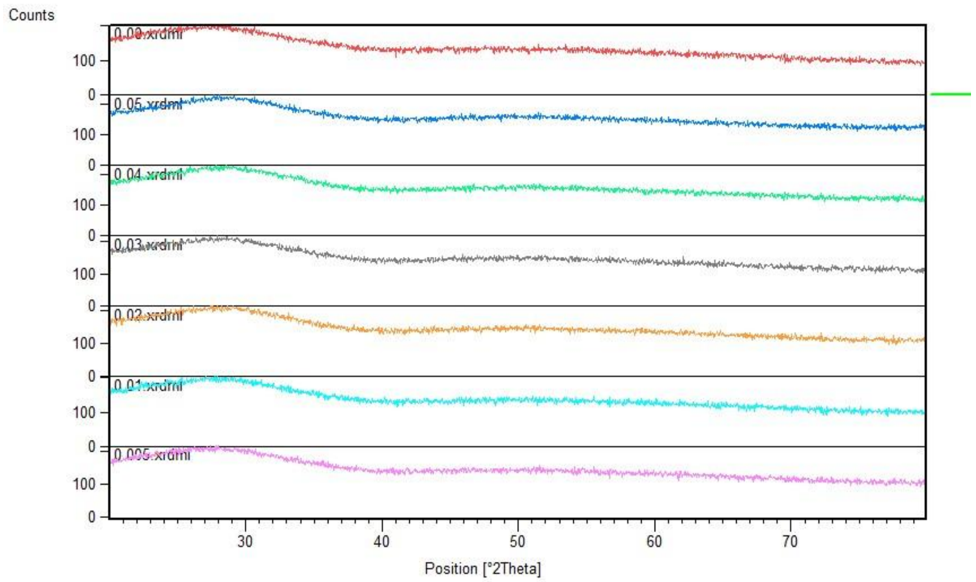

Figure 2: X-ray diffraction pattern of $\{[(TeO_2)_{0.70}\ (B_2O_3)_{0.30}]_{0.7}\ (ZnO)_{0.3}\}_{1-y}\ (Er_3O_2)_y$ glasses

Absorption coefficient

The absorption coefficient can be determined by using the following formula:

$$\alpha\ (\lambda)=2.303\frac{A}{d} \qquad (1)$$

It is shown in Figure 3 that the absorption coefficient decreases with increasing wavelength. The high absorption coefficient among four different compositions for $\{[(TeO_2)_{0.70}\ (B_2O_3)_{0.30}]_{1-x}\ (ZnO)_x\}_{1-y}\ (Er_3O_2)_y$ glasses is y = 0.03 mol% where the absorption coefficient is 2.80 cm^{-1}. However, the lowest absorption coefficient is when y = 0.01 mol% where the absorption coefficient is 5.79 cm^{-1}. The optical absorption edge is not sharply defined in the zinc borotellurite dope erbium glasses, in accordance with their amorphous nature.

According to the Equation (1), the absorption coefficient value is dependent on the observance of the glasses and the thickness of the sample. It is inversely proportional to the thickness of the glass sample. If the sample has large value of the thickness, the absorption coefficient is lower. Therefore, the thickness of each sample is one of the important parameters to obtain the absorption coefficient value. The absorbance of the glass sample also influence on the absorption coefficient with directly proportional behavior to the value of absorption coefficient. It can be seen that the absorption band increasing with increasing mol% of erbium.

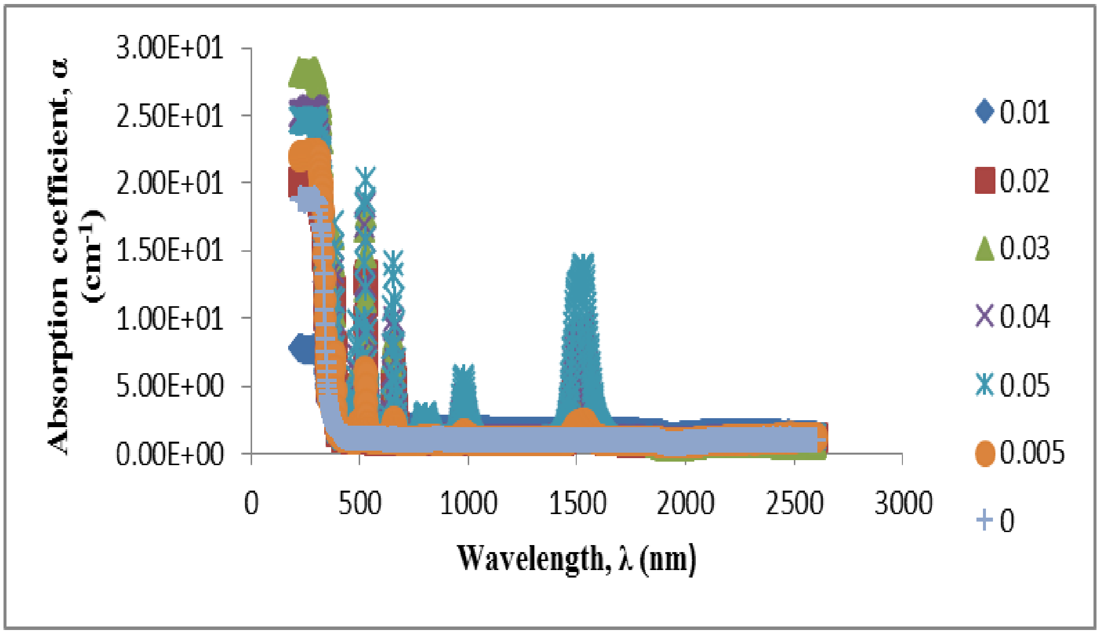

Figure 3: Absorption coefficient for $\{[(TeO_2)_{0.70}\ (B_2O_3)_{0.30}]_{0.7}\ (ZnO)_{0.3}\}_{1-y}\ (Er_3O_2)_y$ glasses

Optical band gap energy (E_{opt}) and Urbach energy (ΔE)

The measurement of optical absorption and the absorption edge is important, especially in connection with the theory of electronic structure of amorphous materials [12]. The study of the optical absorption edge in UV-region has proved to be a very useful method for elucidation of optical transitions and electronic band structure of materials [13].

The values of band gap for direct and indirect transition are shown in Table 1. The Urbach energy (ΔE) for all sample glasses is also presented in Table 1. From Table 1, it is shown that there has non-linear variation in indirect and the direct optical band gap which is due to the variation in the glass structure. The optical band gap values for indirect transition vary between 3.025 and 3.380 eV, while the direct band gap varies from 3.500 to 3.680 eV. The results show that the direct band gap is larger than the indirect band gap. It can be seen that both direct and indirect transitions are involved from the theoretical fitting of the experiment absorption coefficient [14]. The sudden drop of band gap value at 0.01% mol is due to the dual nature of zinc oxide and variations of the non-bridging oxygen in the glass structure. Another possibility could be that the multivalence electron of Er^{2+} that leads to metallization of glasses [15].

The E_{opt} values vary from insulators to semiconductors range, which indicates that increasing concentration of erbium ions causes the structural change in the glass network. The introduction of rare earth materials changes the oxygen bonding in glass forming network and any change of oxygen bonding in the glass network such as the formation of NBO changes the absorption characteristics [12].

When the energy of the incident photon is less than the band gap, the increase in absorption coefficient is followed by an exponential decay of density of states localized into the Gap [16]. The absorption edge here is called Urbach edge. The lack of crystalline long-range order in amorphous/glassy materials is associated with a tailing of density of states into normally forbidden energy [16]. Urbach energy characterizes the extent of the exponential tail of the absorption edge. The absorption edge in many disordered materials follows the Urbach rule given by [17]

$$\alpha(\omega)=B\exp(h\omega/\Delta E) \qquad (2)$$

where B is a constant, ΔE is a measure of the band tailing and is known as the Urbach energy. The values of the Urbach energy ΔE were calculated by taking the reciprocals of the slopes of the linear portion of the ln(α) versus ħω curves in the lower photon energy regions [18]. The Urbach energy is well known that the shape of the fundamental absorption edge in the exponential (Urbach) region can yield information on the disorder affects [19]. Materials with larger Urbach energy would have a greater tendency to convert weak bonds into defects [19]. Table 1, shows that the Urbach energy decreases when erbium content is increased in the sample. The Urbach energy had been determined and lies at around 0.185 and 0.161.The origin of this ΔE can be considered as the cluster of the localized states below the conduction band [12]. From the Urbach energy values, it is confirmed that the phonon-assisted transition exist. From the Urbach energy values, it is confirmed that the phonon-assisted transition occurs. The obtained results are in accordance with those reported for inorganic glasses [20].

Table 1: Indirect optical band gap (E^1_{opt}) , Direct optical band gap (E^2_{opt}) and Urbach energy (ΔE) of $\{[(TeO_2)_{0.70}\ (B_2O_3)_{0.30}]_{0.7}\ (ZnO)_{0.3}\}_{1-y}\ (Er_3O_2)_y$ glasses

Sample, y	E^1_{opt} (eV)	E^2_{opt} (eV)	ΔE(eV)
0.000	3.280	3.600	0.185
0.005	3.348	3.650	0.180
0.010	3.025	3.500	0.200
0.020	3.302	3.622	0.175
0.030	3.262	3.635	0.180
0.040	3.440	3.680	0.161
0.050	3.380	3.650	0.153

CONCLUSIONS

The optical properties of $\{[(TeO_2)_{0.70}\ (B_2O_3)_{0.30}]_{0.7}\ (ZnO)_{0.3}\}_{1-y}\ (Er_3O_2)_y$ glasses have been studied and investigated. The optical and structural properties of the glass samples are dependent on the composition of the glass. The formation of NBO with increase of Er_2O_3 results in the variation of optical energy band gap. This is because NBO binds excited electrons less tightly than bridging oxygen. Both direct and indirect transitions are involved from the theoretical fitting of the experiment absorption coefficient. The optical band gap value for indirect transition varies between 3.025 and 3.440 eV, while direct band gap vary from 3.500 eV to 3.680 eV. From the result, it is noted that the value of Urbach energy does not contribute to the linear variation. The value of Urbach energy is varying between 0.153 eV and 0.200 eV. From the Urbach energy values, it is confirmed that the phonon-assisted transition exists.

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