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IR and UV Spectral Studies of Zinc Tellurite Glasses

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Abstract: A glass system based on TeO₂-ZnO was successfully prepared. The optical properties were investigated using the technique of UV-FTIR spectra. The optical absorption was recorded at room temperature in the wavelength range of 200 to 800 nm while the FTIR spectra were recorded at room temperature in the wave number range 400 to 4000 cm. FTIR analyses reveal that the absorption band, associated with the Te-O-Te vibration mode has been observed near 669 cm⁻¹. From the absorption edge studies, the value of the optical band gap E_{opt} and Urbach tail have been evaluated. The value of E_{opt} lies between 1.88 and 2.62 eV for the indirect transition and for direct transition the values vary from 2.46 to 3.01 eV whereas the Urbach energy values lies between 0.600 to 1.915 eV. The results indicated that the optical properties were observed to be dependent on the ZnO content.

Key words: Tellurite glass, optical band gap, FTIR, urbach energy

INTRODUCTION

Various optical devices with waveguides and ultra fast switching possibilities require efficient nonlinear materials (Berthereau *et al.*, 1994). The best inorganic glasses have a figure of merit substantially higher than any other nonlinear optical material (Vogel *et al.*, 1991). Tellurite glasses are of particular interest because of not only their low transition temperature but also their excellent infrared transmission. Thus they are potential candidates for various longer wavelength application (Sahar and Noordin, 1995; Sahar *et al.*, 1997). Tellurite glasses are also very promising materials for laser and non-linear application in optics due to some of their important characteristic features such as high refractive index, low phonon maxima and low melting temperature (Prakash *et al.*, 2001). Zinc tellurite glasses are reported to be a suitable host for optically active rare earth ions (Sidebottom *et al.*, 1997).

The structure of TeO₂ based glasses is also of interest, because there are two types of basic structure unit, namely TeO₄ trigonal bipyramids (tbp) and TeO₃ trigonal pyramid (tp) (Aida *et al.*, 2000). It has been reported elsewhere (Narazaki *et al.*, 2001) that IR absorption in TeO₂-ZnO glasses is very much depend on the ZnO content. As the amount of ZnO content became higher, the absorption intensity due to the Te-O bond vibration decreases, while the position absorption peak due to the Te-O bonds increases. Several studies (Elkohly and Sharaf, 2001) have dealt with the infrared

absorption spectra of binary tellurite glasses, using the infrared spectroscopy technique.

The study of optical absorption and particularly the absorption is a useful method for the investigation of optically induced transitions and for getting information about the band structure and the energy gap of both crystalline and non crystalline materials (Elkohly and Sharaf, 2001). The principle of this technique is that a photon with the energy greater than the band gap energy will be absorbed. The objective of this study is to report the spectral studies and the optical band gap of the zinc tellurite glass system.

MATERIALS AND METHODS

The binary (ZnO)_x(TeO₂)_{1-x} glasses were prepared by mixing together specific weights of tellurium dioxide (Technical Grade) and zinc oxide ZnO (Alfa Aesar, 99.9%) in a close alumina crucible. The x percentage was ranging from 0.10 to 0.40 mol%. Appropriate amounts of powder chemical were weighed and poured into a crucible. The crucible was covered with a lid and then put inside an electric furnace set at 400°C. The crucible was then transferred to a second furnace set up at 800°C for 60 min. The melt was then poured in a stainless steel cylindrical shaped split mould which had been preheated at 350°C. The prepared samples were cut into required dimension for optical absorption and density measurement. Detailed information on glass preparation can be found elsewhere (Sidek *et al.*, 2004).

The prepared samples were ground into powder form for x-ray diffraction measurement, using X'pert Pro Analytical. The infrared absorption spectra of the studied glass samples were recorded using a Thermo Nicolet FT-IR spectroscopy in conjunction with the KBr disc technique, over the spectral range of 4000-400 cm at room temperature. Glass powdered samples of 2 mg were thoroughly mixed and ground with 200 mg KBr before being pressed into a pellet.

Optical absorption measurements in the wavelength range of 200 to 800 nm were performed at room temperature using a CamSpec MB50 Double Beam UV-Visible Spectrophotometer. The optical absorption coefficient $\alpha(\lambda)$ was calculated from the absorbance A , using the following equation:

$$\alpha(\lambda) = 2.3 A/d$$

Where, d is the thickness of the samples.

RESULTS AND DISCUSSION

The X-ray diffraction experiment show no distinguishable intensity peaks, indicating that the samples were essentially non crystalline or amorphous.

Variations in the density and molar volume with the composition of prepared binary tellurite glasses are shown in Fig. 1. The densities of all glasses increase from 5.098 to 5.283 g cm⁻³ with the substitution of TeO₂ by ZnO, while molar volume decreases from 29.773 to 24.287 cm³ mol⁻¹. The similar behavior has been found by Mallawany (1993). However, the present values are somewhat lower than those found by Mallawany, perhaps due to different preparation technique.

As expected, the increases in densities are due to glass structural change of which the influence of Zn²⁺ on breaking tellurium-oxygen networks (Khozhukharov *et al.*, 1986). In this case, all oxygen atoms from ZnO are used to rupture the Te-O-Te bridges, which accompanied with a change of nearly all participating TeO₄ to TeO₃ groups. These changes might be due to the perturbation of the tellurite of TeO₄ tbp unit into TeO₃ tp unit via intermediate coordination of TeO_{3.5}, (Li *et al.*, 2001; Nazabal *et al.*, 2003; Charton *et al.*, 2003).

To enhance this finding, an attempt has been made to study the structure and the vibrational properties of tellurites by using the Fourier Transform Infra Red (FTIR) technique. The FTIR spectra of the glasses are presented in Fig. 2 and were summarized in the Table 1. As shown in Fig. 2, the absorption peaks occurs at around 669 cm which have been ascribed to the stretching vibration of

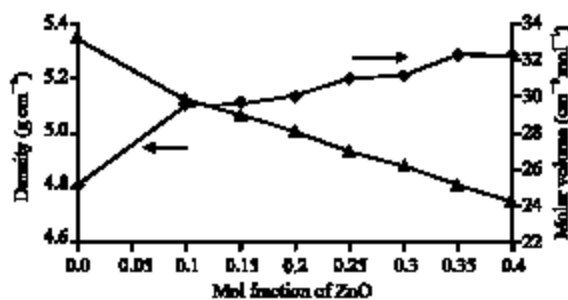


Fig 1: Density and molar volume of (TeO₂)_{1-x} (ZnO)_x glasses

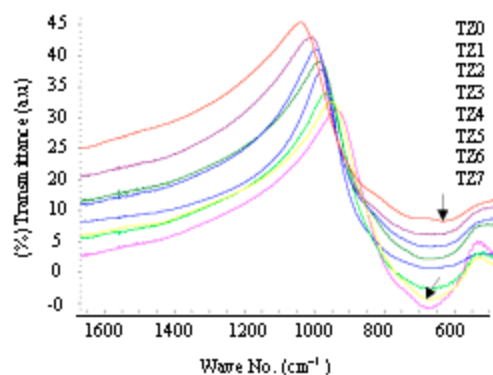


Fig 2: FTIR spectra of (TeO₂)_{1-x} (ZnO)_x glasses with various compositions

Table 1: FTIR peaks position of the (TeO₂)_{1-x} (ZnO)_x glasses

Sample	TeO ₂ ± ZnO	IR bands (cm)
TZ0	100.0±00.0	444; 626
TZ1	90.0±10.0	443; 668
TZ2	85.0±15.0	457; 669
TZ3	80.0±20.0	441; 668
TZ4	75.0±25.0	428; 675
TZ5	70.0±30.0	431; 668
TZ6	65.0±35.0	429; 665
TZ7	60.0±40.0	428; 675

equatorial and axial Te-O bonds in the TeO₄ tbp unit and TeO₃ tp (Sahar and Noordin, 1995). This broad peak also ascribed to the mixing structures of TeO₃ groups, symmetric TeO₄ groups and deformed TeO₄ groups (Hu and Jiang 1996). The peaks shift toward higher wavenumber region as the ZnO content gradually increased. However, the frequency shifts of the peaks are small due to the influence of Zn²⁺ on breaking tellurium-oxygen networks is also small (Sekiya *et al.*, 1994).

The absorption peaks position shift from 443 to 428 cm with the increases of the ZnO content and can be assigned to the Zn-O tetrahedral bond (Liu *et al.*, 1997). It can also noted that a lot of additional small intensity

peaks in the spectra of the glass samples in the range 420-450 cm appear as ZnO content increase. Those small peaks occur due to the deformation of the Te-O bond vibration (Burger *et al.*, 1992).

The optical absorption spectra of TeO₂-ZnO are shown in Fig. 3. It shows the absorption intensity in arbitrary units as a function of wavelength for these glasses. It is clear that there is no sharp absorption edge and this is the characteristic of the glassy state. Generally, the absorption edge of these glasses is determined by the oxygen bond strength in the glass-forming network. Any change of oxygen bonding in the glass network, for instance, the formation of non bridging oxygen, changes the characteristic absorption edge. It is reported that the UV transmittance of ZnO edge shifts to shorter wavelengths with increasing ZnO content in binary tellurite glasses (Burger *et al.*, 1992). In this study, the position of the fundamental absorption edge shifts to

lower energy (higher wavelength) with increasing TeO₂ content in the glass system. Stevels (1953) has suggested that the movement of the ultraviolet absorption band to longer wavelengths corresponds to transitions from the non-bridging oxygen which bound an excited electron less tightly than the bridging oxygen. The general appearance of the absorption spectra of the present glasses is similar to the spectra observed for the same glasses found by Burger (Burger *et al.*, 1992).

The data for Fig. 4 and 6 were obtained from the relation:

$$\alpha(\omega) = \frac{\text{const}}{\hbar\omega} (\hbar\omega - E_{\text{opt}})^n$$

where, E_{opt} is the energy of the optical band gap and $\hbar\omega$ is the photon energy. Values of n are 1/2 and 2 for direct and indirect transitions respectively. Both these band gaps

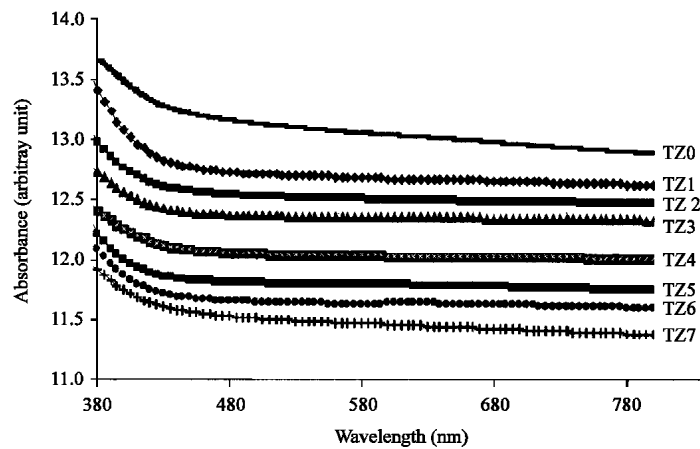


Fig. 3: Optical absorbance spectra for (ZnO)_x(TeO₂)_{1-x} glasses

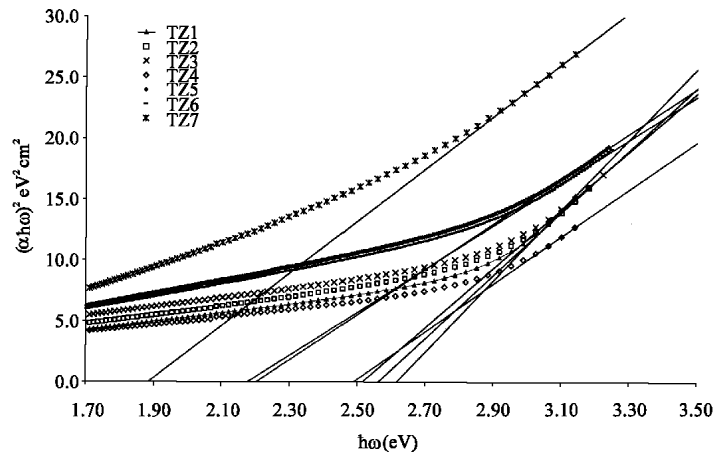


Fig. 4: Plot of $(\alpha\hbar\omega)^2$ against photon energy $\hbar\omega$ for direct band gap measurement

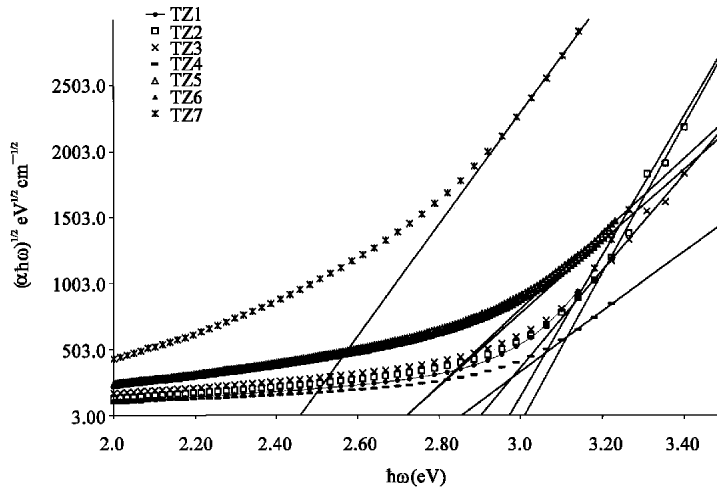


Fig. 5: Plot of $(\alpha h\omega)^{1/2}$ against photon energy $h\omega$ for indirect band gap measurement

Table 2: Direct optical band gap (E^1_{opt}), indirect optical band gap (E^2_{opt}) of $(ZnO)_x(TeO_2)_{1-x}$

Sample	TeO ₂ ± ZnO	E ¹ _{opt} (eV)	E ² _{opt} (eV)	Urbach tail (eV)
TZ1	90.0±10.0	2.973	2.615	0.600
TZ2	85.0±15.0	3.010	2.561	0.707
TZ3	80.0±20.0	2.902	2.514	0.819
TZ4	75.0±25.0	2.854	2.487	0.801
TZ5	70.0±30.0	2.720	2.202	1.454
TZ6	65.0±35.0	2.746	2.176	1.499
TZ7	60.0±40.0	2.458	1.884	1.915

obtained from the above relations are interband transition, but later involve the phonon interaction.

In order to see whether optical data on the present glasses fit better to the direct or indirect band gap formula; data $(\alpha h\omega)^2$ versus $h\omega$ as well as $(\alpha h\omega)^{1/2}$ versus $h\omega$ are plotted in the absorption region as shown in Fig. 4 and 5. Direct or indirect energy band gap is determined from linear regions of the plots as shown in the figures and corresponding values are presented in Table 2. The results show that the direct band gap values are larger than these indirect band gap and both values are decreasing with decrease of TeO₂ content. This result suggests that the covalent nature of the glass matrix decreases with increase of ZnO content.

The variation in the values of optical band gap in the present glass system is shown in Fig. 4 and 5. The values varies from 2.97 to 2.46 eV and from 2.62 to 1.88 eV for $n = 1/2$ and $n = 2$, respectively.

It is known that the concentration of the non-bridging oxygen ions decreases with increasing TeO₂. Figure 6 shows the variation of E_{opt} with composition for ZnO-TeO₂ glasses. The values of E_{opt} decrease linearly with increasing ZnO content. The results in Fig. 6 shows that the variation of E_{opt} with composition can be explained

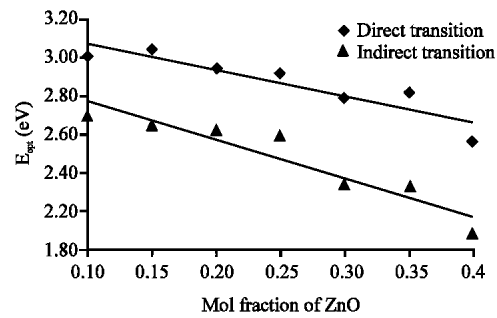


Fig. 6: Variation of optical band gap with glass composition for direct and indirect transition for $(ZnO)_x(TeO_2)_{1-x}$ glasses

by suggesting that the non-bridging oxygen ion content increases with increasing ZnO content, shifting the band edge to lower energies and leading to a decrease in the value of E_{opt} .

In amorphous materials there is a band tailing in the forbidden gap. The extent of this tailing is a measure of the disorder in the material and can be estimated using the Urbach equation as follows (El-Sayed, 2005):

$$\alpha(\omega) = B \exp\left(\frac{h\omega}{\Delta E_t}\right)$$

where, B is a constant and ΔE is the width of the band tail of the electron states. From the slope of the relation between $\ln(\alpha)$ and the $h\omega$ as shown in Fig. 8, the Urbach energy, E_t can be determined. The Urbach energy value for prepared glasses was found to lie between 0.600-1.915 eV (Table 2).

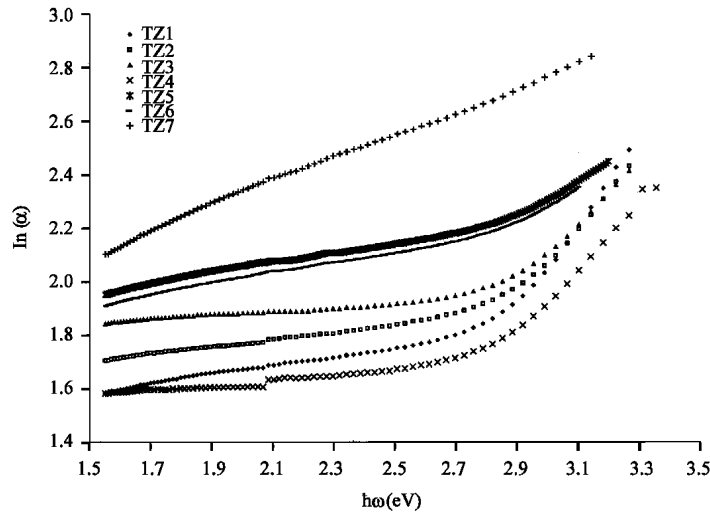


Fig. 7: $\ln(\alpha)$ as a function of $\hbar\omega$ for tellurite glasses

The exponential dependence of absorption coefficient $\alpha(\omega)$ on photon energy ($\hbar\omega$) as shown in Fig. 7 suggests that these materials obey Urbach rule. An addition of TeO_2 to the glass system shows reduction in optical band gap as well as Urbach tails with the densification of the glass network.

CONCLUSION

The spectral studies on the network structure of binary TeO_2 -ZnO glass system revealed the following conclusions:

- The density increases as the ZnO content increases while the molar volume decreases.
- The FTIR spectra for the zinc tellurite glasses of the present studies are in good agreement with earlier works. The sharp absorption peaks of 626 cm^{-1} shifted to 675 cm^{-1} while the absorption peaks around 444- 428 cm^{-1} decreases. These changes might be due to the perturbation of the tellurite of TeO_4 tbp unit into TeO_3 tp unit via intermediate coordination of TeO_{3+1} . The peak observed at about 660 cm^{-1} is assigned to antisymmetric vibrations of Te-O-Te linkages and the peak observed at about 450 cm^{-1} is assigned to symmetric stretching (and bending) vibrations of Te-O-Te linkages which are formed by sharing vertices of TeO_4 tbp's, TeO_{3+1} polyhedra and TeO_3 tp's.
- The optical absorption spectra in the range of 200-800 nm showed that for zinc tellurite glasses, the absorption edge shifted to higher wavelength direction with increasing the TeO_2 content. For direct and indirect forbidden transitions, the optical energy gap (E) was calculated for binary TeO_2 -ZnO glasses.

- The Urbach energy is found to be between 0.600 to 1.915 eV.
- It was found that, the value of E_{opt} decrease with increase ZnO content. The dependence of E_{opt} on ZnO content is most likely related to structural rearrangement in the glass network.

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