Optical and Thermal Properties of Some Tellurite Glasses

Raouf El-Mallawany*, Yasser Saad Rammah, Amin El Adawy, Zahra Wasses

Physics Department, Faculty of Science, Menoufia University, Shebin El-Kom, Egypt

Email address: raoufelmallawany@yahoo.com (R. El-Mallawany)

*Corresponding author

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Abstract: Tellurite glasses in the form (95-x) TeO2-5Nb2O5-xTiO2, x= 5.0, 7.5, 10.0 and 12.5 mol % have been successfully prepared by the melt quenching technique. Density ρ and molar volume V have been measured. UV-Visible absorption spectra for the presented ternary tellurite glass systems have been measured in the wavelength range 200-850 nm. The optical band gap, E_g, and refractive index, n, of the presented glass systems have been calculated by using the derivation absorption spectrum fitting (DASF) and absorption spectrum fitting (ASF) methods. Also, Urbach’s energy, ΔE for tellurite glass systems was obtained using the absorption spectrum fitting (ASF) method. Comparison between both methods has been presented. Differential thermal analysis (DTA) for the prepared glasses with systematic heating rate 10°C/min has been carried out. The glass transition temperature, T_g, onset crystallization temperature, T_c, melting temperature, T_m, glass stability range, S, and glass factor, K_g, of the present glasses have been measured. The average cross-link density, n_c, number of bonds per unit volume, n_b, and average stretching force constant, F, have been calculated.

Keywords: Glass, Tellurite, Optical, Thermal

1. Introduction

Physical and structural investigations of tellurite glasses have been studied with different transition metal oxides TMO and rare earth oxides REO compositions [1-10]. Recently, self-cleanness of co-doped lithium niobate tellurite glass and UV converted white light-emitting diodes (W-LEDs) have been reported [1, 4]. In Tauc’s method [11, 12], absorption coefficient (α) requires measurement of the absorbance, reflectance, and thickness of the film. Recently, the absorption spectrum fitting method (ASF) and derivation of absorption spectrum fitting (DASF) methods have been introduced to obtain the band gap avoiding the film thickness measurement which commonly could not be measured precisely [13,14]. Also, tellurite glasses with high thermal and glass stabilities were suggested as potential materials to realize highly efficient fibers [15-20].

The present goal is to prepare new tellurite glass system and measure both UV spectra and thermal properties. The (E_g), (E_a) and (n) were calculated using both (ASF) and (DASF) methods. Glass transition temperature, T_g, onset crystallization temperature, T_c, melting temperature, T_m, glass stability range, S, and glass factor, K_g were determined. Quantitative analysis of the experimental results will be based on the average crosslink density and the average stretching force constant in the glass.

2. Experimental Work

Tellurite glasses in the form (95-x) TeO2-5Nb2O5-xTiO2, x= 5.0, 7.5, 10.0 and 12.5 mol % have been prepared by melt quenching technique as in Table 1. High purity oxides 99.99% have been used to prepare the present glasses. Each batch was transferred to alumina crucible and melted at 800-1000°C in the melting furnace for 10 minutes. The melt stirred to achieve desirable homogeneity and poured on a preheated stainless steel mold to avoid thermal shocks and annealed for 1 hour at 250°C to release the mechanical strains. Density of every glass was measured at room temperature (23-25°C) by the Archimedes’ method by using acetone as the immersion liquid. Molar volume is calculated by the next equation:
3. Results and Discussion

All the glasses were transparent, bubble-free, and homogeneous. The XRD patterns of the present glasses showed no sharp peaks which confirmed amorphous property. The density of the present glass decreased from 2.71 to 2.47 g/cm$^3$ and molar volume increased from 58.055 to 63.24 cm$^3$ due to the increase of TiO$_2$ from 5 to 12.5 mole % as in Table 1. Figure 1 shows UV-Vis spectra for glassy system (95-x)TeO$_2$-5Nb$_2$O$_5$-xTiO$_2$, x= 5.0, 7.5, 10.0, 12.5 mol %.

Table 1. Tellurite glass composition, ρ and V of (95-x)TeO$_2$-5Nb$_2$O$_5$-xTiO$_2$, x= 5.0, 7.5, 10.0 and 12.5 mol %.

| (95-x)TeO$_2$-5Nb$_2$O$_5$-xTiO$_2$ mol % | ρ (g/cm$^3$) | V (cm$^3$) |
|-----------------------------------------|-------------|-----------|
| 90TeO$_2$-5Nb$_2$O$_5$-5TiO$_2$          | 2.71        | 58.055    |
| 87.5TeO$_2$-5Nb$_2$O$_5$-7.5TiO$_2$      | 2.59        | 59.129    |
| 85TeO$_2$-5Nb$_2$O$_5$-10TiO$_2$         | 2.50        | 62.78     |
| 82.5TeO$_2$-5Nb$_2$O$_5$-12.5TiO$_2$     | 2.47        | 63.24     |

Optical band gap $E_g$ and Urbach energy $\Delta E$ values were evaluated by using next equation [12, 21, 22].

$$\alpha(\nu) = A (h\nu - E_g)^n$$

(2)

where $E_g$ (eV) is the optical band gap energy, $A$ is a constant, the exponent $n$ takes different values depending on the mechanism of inter band transitions. The Urbach energy [22] is given by

$$\alpha(\nu) = \alpha_0 \exp \left( \frac{h\nu}{\Delta E} \right)$$

(3)

Where $\alpha_0$ is constant and $\Delta E$ is the width of the band tails.

Figure 2 represented the (DASF) [14], $d(\ln[A(\lambda)/\lambda])/(d(1/\lambda))$ versus (1/λ) for the present glass samples. The optical energy gap will be calculated according to the (DASF) model [14] by using relations (4-6):

$$E_g = \frac{hc}{\lambda_g}$$

(4)

$$E_g = \frac{hc}{\lambda_g}$$

(5)

$$\Delta E = 1239.83/slope$$

(6)

Where $h$ is Planck’s constant and $c$ is the velocity of the light and the values of Urbach energy, $\Delta E$ in eV can be obtained in the (DASF) method [14] from the slope of the linear region of the ln $(A/\lambda) - (1/\lambda)$ curves as shown in Figure 2 (A, B, C, D). The optical energy gap will be calculated by using Eq.(4). The DASF and ASF methods show a change in the slope at 1/λ=1/λ$_g$ and $E_{opt}$ (eV) can be determined for every glass systems using Eq. (4,5). Figure 3 shows the change of $(A/\lambda)^{0.5}$ against (1/λ). Values of Urbach energy $\Delta E$ (eV) can be calculated from the slope of the linear region of the ln $(A/\lambda)^{0.5} - (1/\lambda)$ curves using Eq.(3) as shown
in figure 4. Table 2 and figure 5 show that there is agreement between the $E_g$ obtained from ASF, DASF, and Davis and Mott methods.

**Table 2.** $E_{opt}$ and $\Delta E$ by the (DASF) and (ASF) for tellurite glasses (95-x)TeO$_2$-5Nb$_2$O$_5$-xTiO$_2$ and x= 5.0, 7.5, 10.0, 12.5 mol %.

| TiO$_2$ mole % | DASF method | ASF method |
|----------------|-------------|------------|
|                | $E_g$ (eV) Eq.(5) | Indirect $E_g$ (eV) Eq. (6) | Direct $E_g$ (eV) Eq. (6) | $\Delta E$ (eV) Eq. (7) | Refractive Index Eq. (8) |
| 5.0            | 3.06        | 2.91       | 3.09       | 0.21       | 2.42       |
| 7.5            | 5.29        | 4.95       | 5.14       | 0.51       | 2.00       |
| 10.0           | 3.07        | 4.09       | 4.15       | 0.14       | 2.15       |
| 12.5           | 2.96        | 3.31       | 3.34       | 0.28       | 2.31       |

The refractive index is calculated for all samples by the next equation [23]:

\[
\left( \frac{n^2-1}{n^2+2} \right) = 1 - \frac{E_g}{\sqrt{20}}
\]

Values of the calculated refractive index by both ASF and DASF methods were collected in Table 2 and represented in figure 6. The $E_g$ has a maximum and refractive index has a minimum at 7.5 TiO$_2$ mole %.
Figure 2. $d\ln[A(\lambda)/\lambda]/d(1/\lambda)$ versus $(1/\lambda)$ for $(95-x)\text{TeO}_2-5\text{Nb}_2\text{O}_5-x\text{TiO}_2$, $x=5.0, 7.5, 10.0, 12.5$ mol % in the wavelength range of 380-500 nm.
Figure 3. The indirect $E_{opt}$ by the absorption spectrum fitting (ASF) for (95-x)TeO$_2$-5Nb$_2$O$_5$-xTiO$_2$, x = 5.0, 7.5, 10.0, 12.5 mol %; A, B, C, and D for $\text{TiO}_2$ = 5.0, 7.5, 10.0, 12.5 mol %, respectively.
Differential thermal analyzer (DTA) data for the current samples with different TiO$_2$ is presented in Table 3. The increase of TiO$_2$ in the presented glass systems increases $T_g$ from 370 to 420°C, $T_c$ from 513 to 596°C, $T_m$ from 750 to 800°C and $S$ from 143 to 176°C, respectively. Parameter $K_g$ increased from 0.6 to 0.86 which is higher than the value for pure TeO$_2$ (0.41) [25]. The $T_g$ is an increasing function of both $n_c$ and $F$ [25]:

**Figure 4.** The direct optical energy gap by the absorption spectrum fitting (ASF) for (95-x)TeO$_2$-5Nb$_2$O$_5$-xTiO$_2$, x = 5.0, 7.5, 10.0, 12.5 mole %; A, B, C, and D for TiO$_2$ = 5.0, 7.5, 10.0, and 12.5 mol%, respectively.

**Figure 5.** Energy gap $E_g$ values for (95-x)TeO$_2$-5Nb$_2$O$_5$-xTiO$_2$, x = 5.0, 7.5, 10.0, 12.5 mol % calculated by different methods.

**Figure 6.** Refractive index, $n_c$ for (95-x)TeO$_2$-5Nb$_2$O$_5$-xTiO$_2$, x = 5.0, 7.5, 10.0, 12.5 mol % in different methods.

**Table 3.** The thermal and structural factors the present tellurite glasses with different TiO$_2$ contents; $T_g$, $T_c$, $T_m$, $S$, $K_g$, $n_c$, $F$ and $n_b$ for (95-x) TeO$_2$-5Nb$_2$O$_5$-xTiO$_2$, x = 5.0, 7.5, 10.0 and 12.5 mol %.

| TiO$_2$ mole% | $T_g$ (°C) | $T_c$ (°C) | $T_m$ (°C) | S (°C) | $K_g$ | $n_c$ | $n_b \times 10^4$ (m$^{-3}$) | F (N/m) |
|---------------|------------|------------|------------|--------|------|------|----------------------------|---------|
| 5             | 370        | 513        | 750        | 143    | 0.6  | 2.64 | 8.97                      | 245.19  |
| 7.5           | 384        | 550        | 772        | 166    | 0.74 | 2.67 | 9.32                      | 244.78  |
| 10            | 399        | 570        | 788        | 171    | 0.78 | 2.71 | 9.59                      | 244.30  |
| 12.5          | 420        | 596        | 800        | 176    | 0.86 | 2.74 | 9.87                      | 243.94  |
where, \( n^*_c \) is the average cross-link density and calculated from:

\[
\bar{n}_c = \frac{\sum x_i (n_c/\langle N_c \rangle)_i}{\sum x_i (n_c/\langle N_c \rangle)_i}
\]

(9)

where \( N_c \) is the number of cations per glass formula unit, \( x \) is the mole fraction of component oxide and \( i \) denote the component oxide.

\( F^* \) is the average stretching force constant of the glass [25],

\[
\bar{F} = \frac{\sum (x_c f_i)/\langle N_c \rangle_i}{\sum (x_c f_i)/\langle N_c \rangle_i}
\]

(10)

\[ f = 17 / r^3 \]

(11)

where \( f \) is the first order stretching force constant and \( r \) is the cation radius in Angstrom.

The present data will be added to other data of tellurite glasses [26-32] to make the behavior of these special glasses clear.

4. Conclusion

Tellurite glasses in the form \((95-x)\ TeO_2-5\ Nb_2O_5-x\ TiO_2, x = 5.0, 7.5, 10.0 and 12.5\) mol % have been achieved. It is concluding that that there is a good agreement between the values obtained from ASF and DASF analysis for UV spectra. The increase of TiO_2 in the presented glass systems increases \( T_g \) from 370 to 420°C, \( T_c \) from 513 to 596°C, \( T_m \) from 750 to 800°C and S from 143 to 176°C, respectively.

Compliance with Ethical Standards

The authors declare that they have no conflict of interest.

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