

Optical and Thermal Properties of Some Tellurite Glasses

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Abstract: Tellurite glasses in the form $(95-x)\text{TeO}_2-5\text{Nb}_2\text{O}_5-x\text{TiO}_2$, $x=5.0, 7.5, 10.0$ 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 $10^\circ\text{C}/\text{min}$ 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, \bar{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-cleanliness 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^{opt}), (E_g) 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 $(95-x)\text{TeO}_2-5\text{Nb}_2\text{O}_5-x\text{TiO}_2$, $x=5.0, 7.5, 10.0$ 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 $800-1000^\circ\text{C}$ 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 1hour at 250°C to release the mechanical strains. Density of every glass was measured at room temperature ($23-25^\circ\text{C}$) by the Archimedes' method by using acetone as the immersion liquid. Molar volume is calculated by the next equation:

$$V = \frac{M_{w\text{glass}}}{\rho_{\text{glass}}} \quad (1)$$

Where $M_{w\text{glass}}$ is the molecular weight and ρ_{glass} is the density of the glass samples. A Perkin-Elmer 402 double beam spectrophotometer has been used to measure the UV-Vis absorption spectra of the polished glass samples in the range 200-850 nm. T_g , T_c and T_m have been measured by using (DTA) apparatus (DTA-50, SHIMADZU, Japan, Nitrogen rate 30 ml/min) by using glass powders in platinum tubes in the temperature range 30-900°C with heating rate 10°C/min.

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/cm³ and molar volume increased from 58.055 to 63.24 cm³ due to the increase of TiO₂ from 5 to 12.5 mole % as in Table 1. Figure 1 shows UV-Vis spectra for glassy system (95-x)TeO₂-5Nb₂O₅-xTiO₂, x= 5.0, 7.5, 10.0, 12.5 mol %.

Table 1. Tellurite glass composition, ρ and V of (95-x)TeO₂-5Nb₂O₅-xTiO₂, 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
85 TeO 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

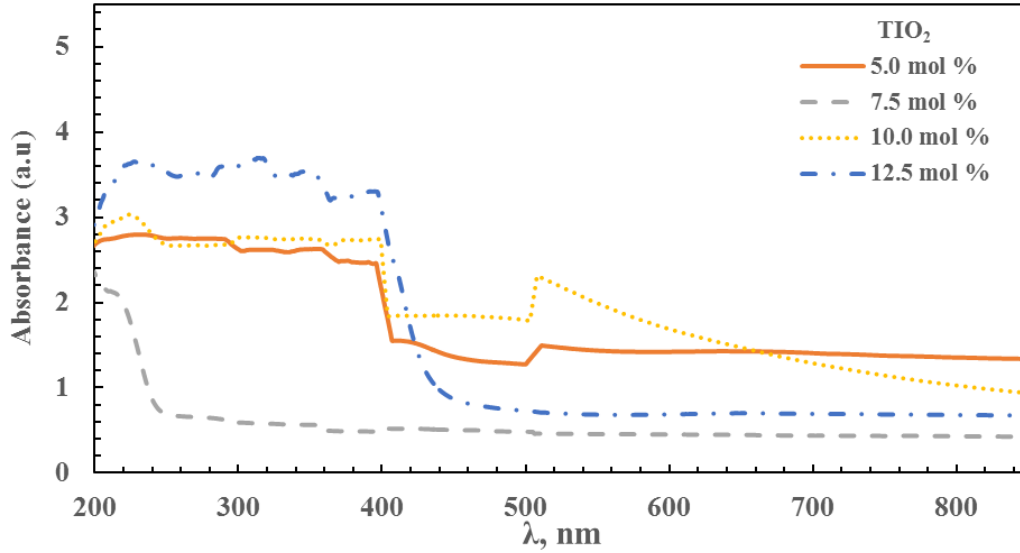


Figure 1. Optical absorption spectra for tellurite glasses (95-x)TeO₂-5Nb₂O₅-xTiO₂, x= 5.0, 7.5, 10.0, 12.5 mol%.

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

$$\alpha(\nu) = \frac{A(h\nu - E_g)^n}{h\nu} \quad (2)$$

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

$$\alpha(\nu) = \alpha_o \exp\left[\frac{h\nu}{\Delta E}\right] \quad (3)$$

Where α_o is constant and ΔE is the width of the band tails. Figure 2 represented the (DASF) [14], $d\{\ln[A(\lambda)/\lambda]\}/d(1/\lambda)$ versus $(1/\lambda)$ for the present glass samples. The optical energy gap will be calculated according to the (DASF) model [14] by using relations (4-6):

$$E_{gap}^{DASF} = \frac{hc}{\lambda_g} = \frac{1239.83}{\lambda_g} \quad (4)$$

$$E_{gap}^{ASF} = \frac{hc}{\lambda_g} = \frac{1239.83}{\lambda_g} \quad (5)$$

$$\Delta E = 1239.83/\text{slope} \quad (6)$$

Where h is Planck's constant and c is the velocity of the light and the values of Urbach energy, ΔE 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 $1/\lambda = 1/\lambda_g$ 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 $(1/\lambda)$. Values of Urbach energy ΔE (eV) can be calculated from the slope of the linear region of the $\ln(A/\lambda)^2 - (1/\lambda)$ 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.

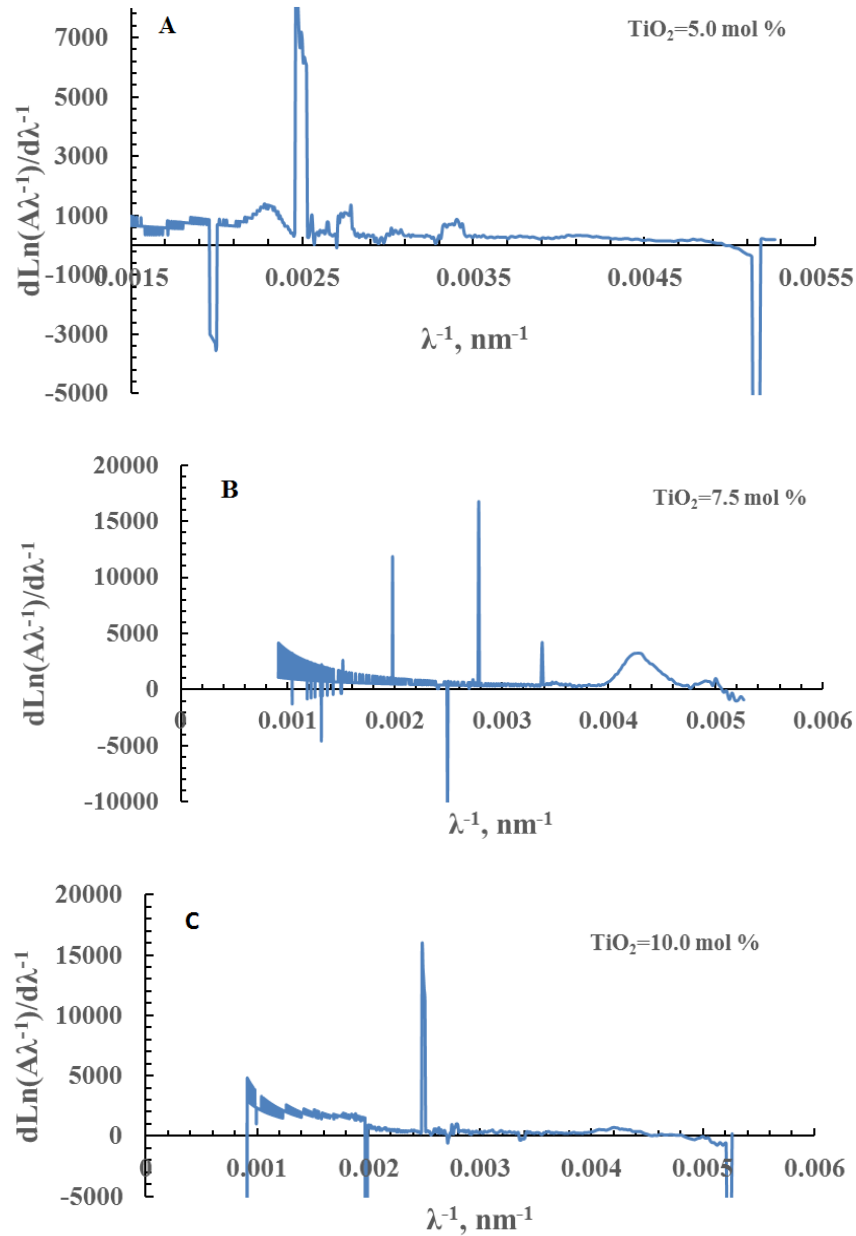
Table 2. E_{opt} and ΔE by the (DASF) and (ASF) for tellurite glasses $(95-x)\text{TeO}_2-5\text{Nb}_2\text{O}_5-x\text{TiO}_2$ and $x=5.0, 7.5, 10.0, 12.5$ mol %.

TiO ₂ mole %	DASF method		ASF method			
	E_g (eV) Eq.(5)	Refractive Index Eq. (8)	Indirect E_g (eV) Eq. (6)	Direct E_g (eV) Eq. (6)	ΔE (eV) Eq. (7)	Refractive Index Eq. (8)
5.0	3.06	2.38	2.91	3.09	0.21	2.42
7.5	5.29	1.95	4.95	5.14	0.51	2.00
10.0	3.07	2.37	4.09	4.15	0.14	2.15
12.5	2.96	2.40	3.31	3.34	0.28	2.31

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

$$\left(\frac{n^2-1}{n^2+2}\right) = 1 - \sqrt{\frac{E_g}{20}} \quad (7)$$

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 TiO₂ mole %.



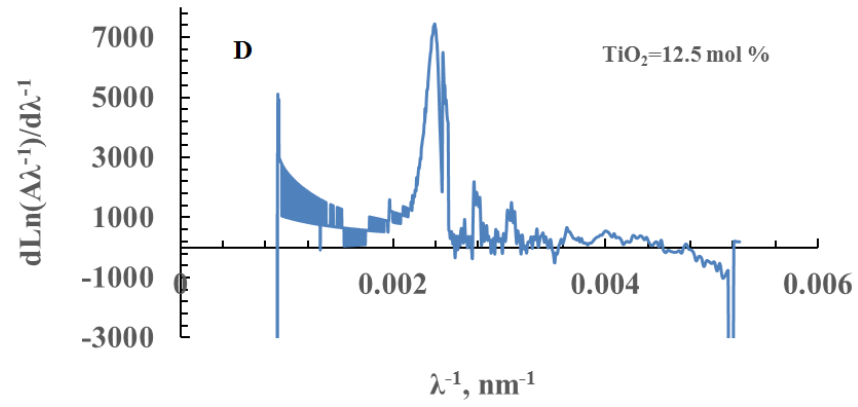
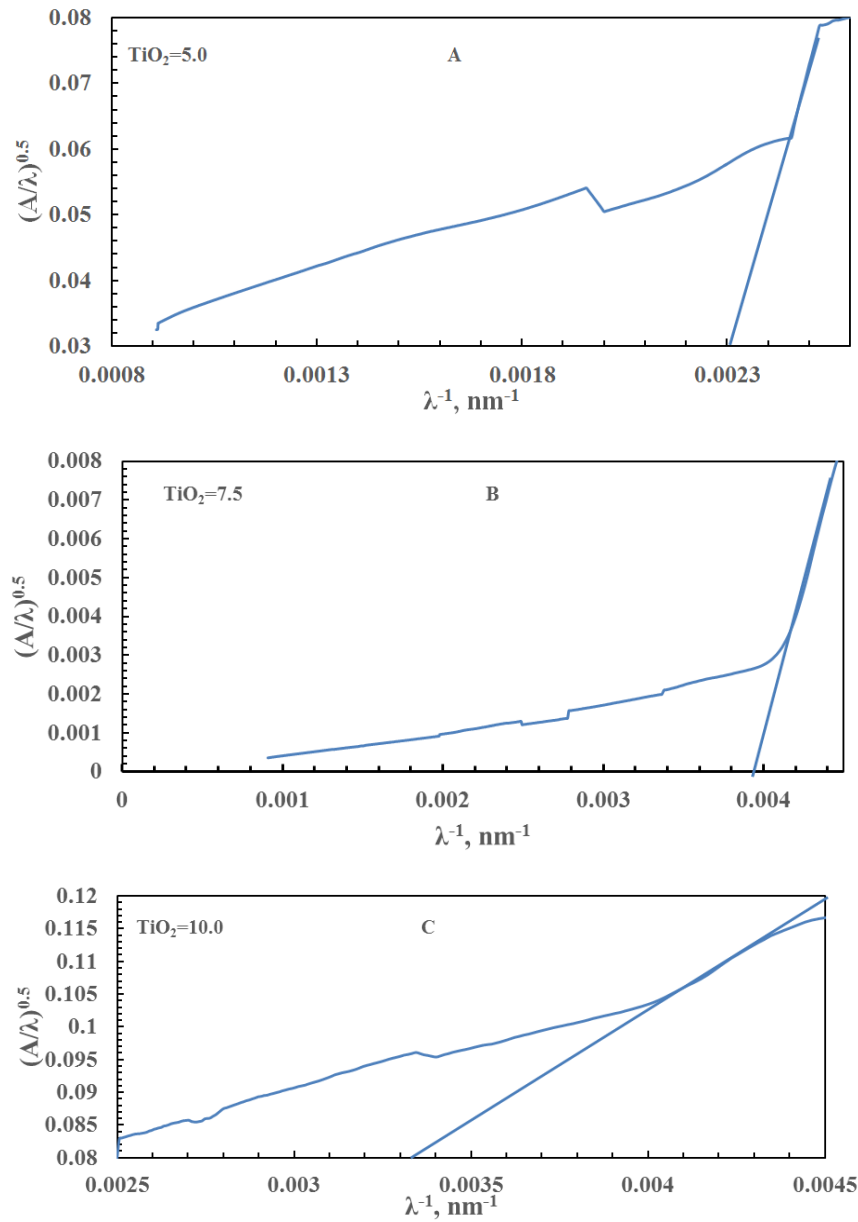


Figure 2. $d\{\ln[A(\lambda)/\lambda]\}/d(1/\lambda)$ versus $(1/\lambda)$ for $(95-x)\text{TeO}_2-5\text{Nb}_2\text{O}_5-x\text{TiO}_2$, $x=5.0, 7.5, 10.0, 12.5 \text{ mol \%}$ in the wavelength range of 380-500nm.



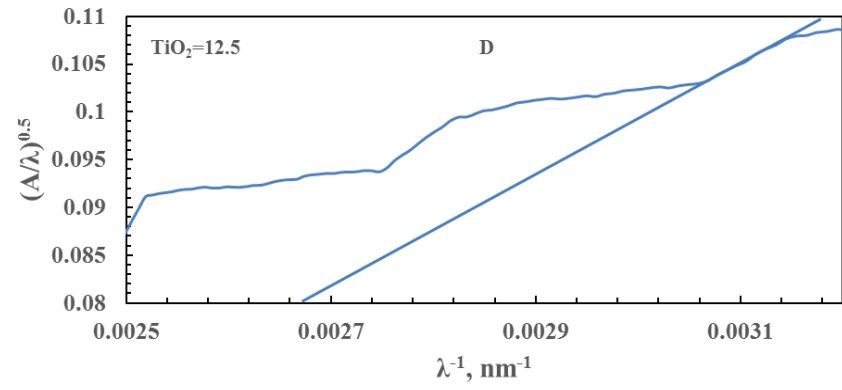
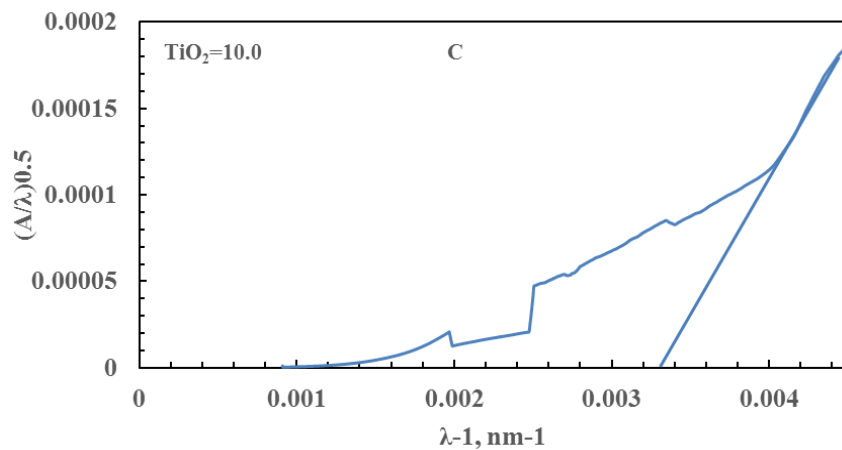
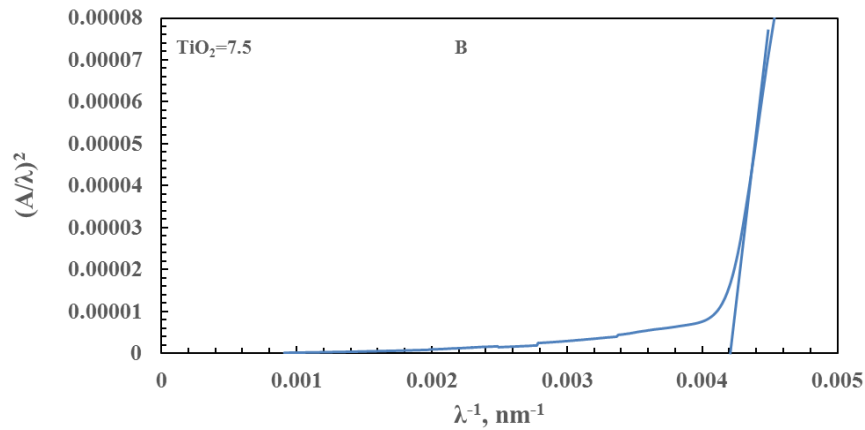
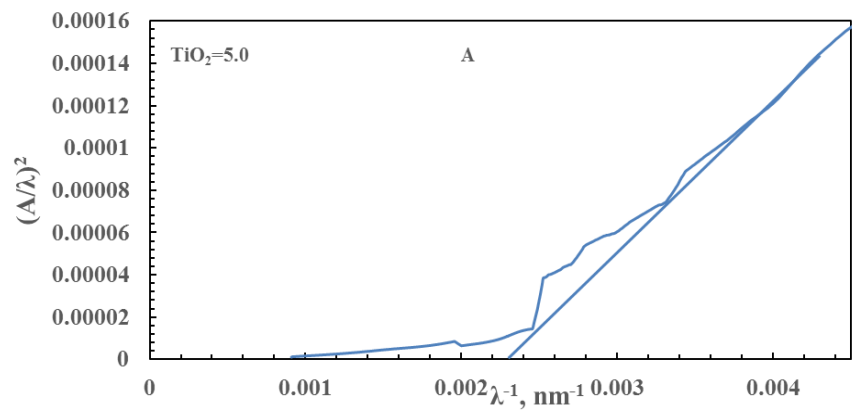


Figure 3. The indirect E_{opt} by the absorption spectrum fitting (ASF) for $(95-x)\text{TeO}_2-5\text{Nb}_2\text{O}_5-x\text{TiO}_2$, $x=5.0, 7.5, 10.0, 12.5$ mol %; A, B, C, and D for $\text{TiO}_2=5.0, 7.5, 10.0, 12.5$ mole%, respectively.



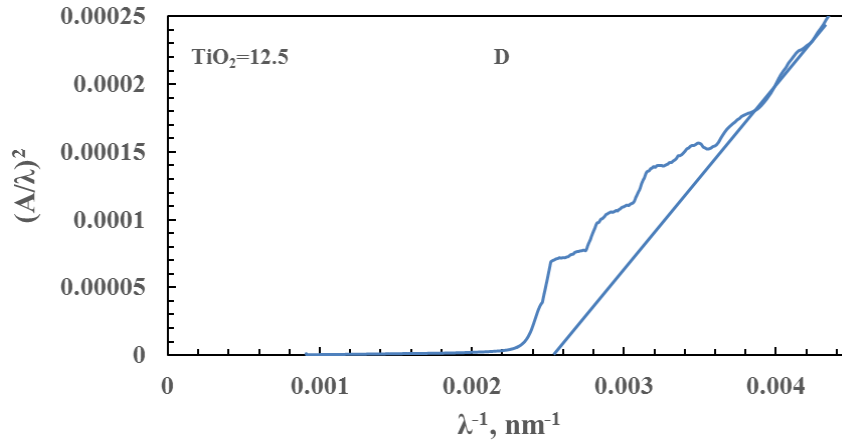


Figure 4. The direct optical energy gap by the absorption spectrum fitting (ASF) for $(95-x)\text{TeO}_2-5\text{Nb}_2\text{O}_5-x\text{TiO}_2$, $x=5.0, 7.5, 10.0, 12.5$ mole %; A, B, C, and D for $\text{TiO}_2=5.0, 7.5, 10.0$, and 12.5 mol%, respectively.

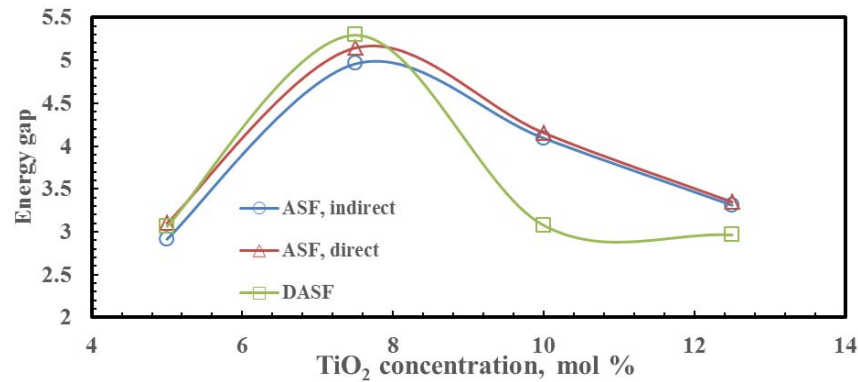


Figure 5. Energy gap E_g values for $(95-x)\text{TeO}_2-5\text{Nb}_2\text{O}_5-x\text{TiO}_2$, $x=5.0, 7.5, 10.0, 12.5$ mol % calculated by different methods.

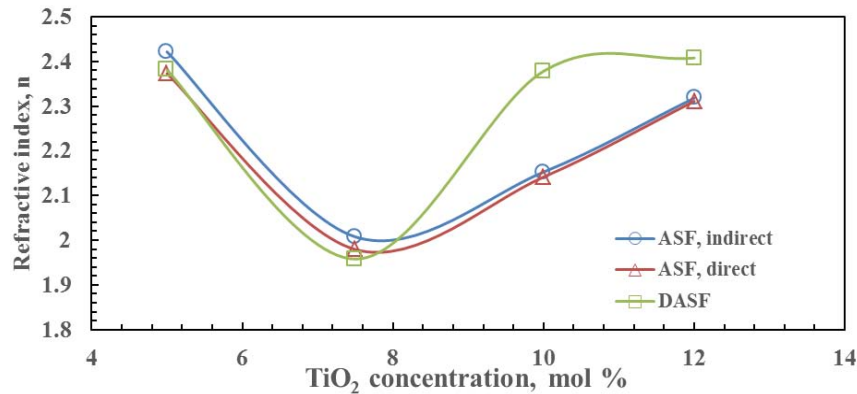


Figure 6. Refractive index, n for $(95-x)\text{TeO}_2-5\text{Nb}_2\text{O}_5-x\text{TiO}_2$, $x=5.0, 7.5, 10.0, 12.5$ mol % in different methods.

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 , \bar{n}_c , F^- and n_b for $(95-x)\text{TeO}_2-5\text{Nb}_2\text{O}_5-x\text{TiO}_2$, $x=5.0, 7.5, 10.0$ and 12.5 mol %.

TiO_2 mole%	T_g (°C)	T_c (°C)	T_m (°C)	S (°C)	K_g	\bar{n}_c	$N_b \times 10^{28} (\text{m}^{-3})$	$F^- (\text{N/m})$
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

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 \bar{n}_c and F^- [25]:

$$T_g = f(\bar{n}_c, \bar{F}) \quad (8)$$

where, \bar{n}_c is the average cross-link density and calculated from:

$$\bar{n}_c = \frac{\sum_i x_i (n_c) i (N_c) i}{\sum_i x_i (N_c) i} \quad (9)$$

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.

\bar{F} is the average stretching force constant of the glass [25],

$$\bar{F} = \frac{\sum_i (x_n f) i}{\sum_i (x_n) i} \quad (10)$$

$$f = 17 / r^3 \quad (11)$$

where f is the first order stretching force constant and r is the cation radius in Angstrom. The increase of TiO_2 concentration from 5-12.5 mole % in the presented glass system leads to increase in the average cross-link density \bar{n}_c from 2.64 to 2.74 and decrease in the average stretching force constant \bar{F} from 245.19 to 243.94, which is consistent with T_g increase. The number of bonds per unit volume of the presented glass systems, n_b , was calculated using the next relation:

$$n_b = N_A / V_m \sum_i (n_f x) i \quad (12)$$

where N_A is Avogadro's number and V_m is molar volume of the glass. The n_b increased from 8.97 to $9.87 \times 10^{28} \text{ m}^{-3}$ due to the increase of TiO_2 from 5 to 12.5 mole%. The number of bonds per unit volume of the present glasses are greater than that for TeO_2 glass ($7.74 \times 10^{28} \text{ m}^{-3}$) [25] and revealed that the present glasses are more bonded ternary glass networks. 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 $(95-x) \text{TeO}_2\text{-}5\text{Nb}_2\text{O}_5\text{-}x\text{TiO}_2$, $x = 5.0, 7.5, 10.0$ and $12.5 \text{ mol } \%$ have been achieved. It is concluding 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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