Physical characterization of Titania modified sodium borate glasses

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Sodium borate glasses modified with TiO_2 were prepared and investigated with UV spectroscopy and DTA. The results indicated some structural modification of the borate network as the TiO_2 content increases. The UV transmission decreases while the UV absorption increases, which increases the refractive index and the optical energy band gap. Also, the detected bulk modulus along with the T_g decrease. Introducing TiO_2 in the glass network resulted in an increase in coordination number of the glass, so the concentration of its basic structural unit TiO_6 units will increase resulting in the creation of more NBOs. This process was attributed to the increase of the density, the third-order nonlinear optical susceptibility ($\chi^{(3)}$) and the fragility of the glasses which decreased the rigidity.

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1. Introduction

B_2O_3 based glasses were containing extensive fields of applications include: optical glasses [1], high capacity reversible electrodes [2], gamma ray-shielding [3], inhibiting bacterial growth [4], textile or continuous filament fiber glass [5] and recently as bioactive material [6-7]. The addition of a member of 3d transition metal oxides such as TiO_2 to borate based glasses is considered as a nucleating agent in some special glasses for electrical, optical and can be served as a nucleating agent which ensures bulk crystallization [1, 4]. The borate anomalous along with the addition of TiO_2 can be utilized to enhance the thermal parameters. This enhancement can be achieved by correlating these parameters with the structure of the glasses containing TiO_2 [8-9]. It was assumed before that titanium ion can exhibit two valence states in the structure of the glass depending on its concentration and the condition of melting. The two valence states are trivalent and / or tetravalent ions. In the case of alkali borate glasses, the colorless high tetravalent (Ti^{4+}) ions were manifested itself [10-11]. Recent studies on the thermal behavior of titanium containing borate glass–ceramics, for example, $BaTiO_3$ and $PbTiO_3$ have shown great potential in certain electronic applications due to their high dielectric properties [12-15]. Also, TiO_2 crystallized borate glasses were prepared by melting and quenched followed by heat treatment, and the fabricated titania crystallized glass could be not only a photo catalytic material but also a promising candidate for random lasing devices.

On the basis of the aforementioned aspects, the main goal of this work is the investigation of the role of a TiO2 addition to the glass transition temperature (T_g), optical band gap (E_g) and the refractive index of Na_2O – B_2O_3 glasses.

2. Experimental procedures

Glasses of the B_2O_3-Na_2O-TiO_2 system were prepared from laboratory reagent grades of Analar Na_2CO_3, H_3BO_3, and TiO_2 by heating the mixture in an electric furnace at 1200 ^{0}C in a platinum crucible, followed by quenching the melt in the air at the room temperature. The glass melts were stirred occasionally with an alumina rod to ensure homogeneous melts. This procedure was used to prepare the glasses with the formula 80 B_2O_3 – 20 Na_2O (wt. %) – x TiO_2 (x= 0, 0.5, 1, 3 and 5 gm) (Nominal compositions). The compositions of the studied samples were listed in Table 1.

Table 1. The nominal glass composition of the glass system Na_2O – B_2O_3 –TiO_2

Glass	Na_2O	B_2O_3	TiO_2
		wt %	
g1	20	80	0.0
g2	20	79.5	0.5
g3	20	79	1.0
g4	20	77	3.0
g5	20	75	5.0

The amorphous nature of the glass samples was inspected by using a Philips X-ray diffractometer PW/1710 with Ni-filtered, Cu-K_α radiation (λ = 1.542 Å)

powered at 40 kV and 30 mA. The glass density of the as-prepared glasses was determined by Archimedes method.

Differential thermal analysis (DTA) of glass powder was carried out using a differential thermal analyzer (type Shimadzu 50) with an accuracy of ±0.1 K. The glass powders, weighing 20 mg, were contained in an alumina crucible and the reference material was α-alumina. The samples were heated in air at heating rates β of 2.5, 5, 10, 20, and 40 K/min. The glass transition temperature T_g, the crystallization peak temperature T_p, and the melting temperature T_m, were determined with an accuracy of ± 1 K from DTA thermograms.

The transmittance (T) and the absorption (A) optical spectra of the prepared glasses were recorded at room temperature in the wavelength range 200–3000 nm by using a computerized double beam spectrophotometer, type JASCO- 630 V. The accuracy to which λ and T can be measured is ±1 nm and ±0.3%, respectively.

3. Results and discussion

The amorphous nature of the studied glass samples was checked by X-ray diffraction techniques. The XRD showed no significant or sharp peaks, so all synthesized samples are in the amorphous state.

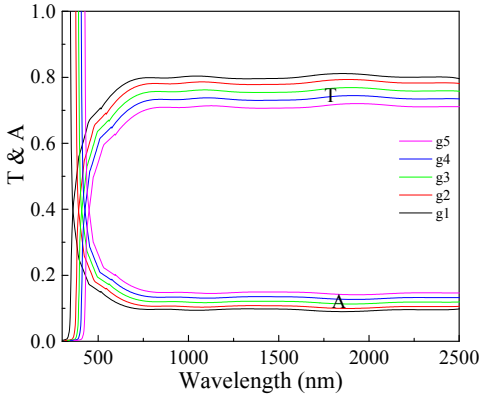

Fig. 1. Spectral behavior of transmittance and absorbance of the glass system $Na_2O - B_2O_3 - TiO_2$

Fig. 1 shows the optical transmission (T) and absorption (A) spectra for B_2O_3-Na_2O-TiO_2 glasses. As shown in this figure the glass transmission decreases while the absorption increases with increasing of TiO_2 content. It was reported earlier [16] that, the ratio 80 B_2O_3 - 20 Na_2O (wt.%) is near the stoichiometric ratio of binary sodium borate glasses. Thus, the addition of a transition metal oxide [17] converts some low density [BO_3] into high density [BO_4] structural units. Moreover, B_2O_3 had a lower density than that of TiO_2 which incorporated in the increase of the density which in its turn increases the absorption and decrease the transmittance according to the theory of reflectivity of light [18-19]. According to other work elsewhere [1,4], TiO_2 is a nucleating agent, i.e., its existence may create small crystals incorporated in the increase of the density and hence, increase the absorption of light and decrease its transmission. A similar behavior was noticed by Morsi et al. [20] in an optical study of borate glasses containing TiO_2 in a relation to its structure. The values of the density of the studied glasses were listed in Table 2. The optical absorption coefficient (α) for B_2O_3-Na_2O-TiO_2 glasses was evaluated using the following relation ($\alpha = A\ d^{-1}$) where d is the thickness of the glass and the relation was represented in Fig. 2. According to Pankove [21], the indirect optical band gap energy (E_g) can be obtained based on the following equation:

$$\alpha\hbar\omega = B\ (\hbar\omega - E_g)^2 \quad (1)$$

where B is a constant and $\hbar\omega$ is the incident photon energy.

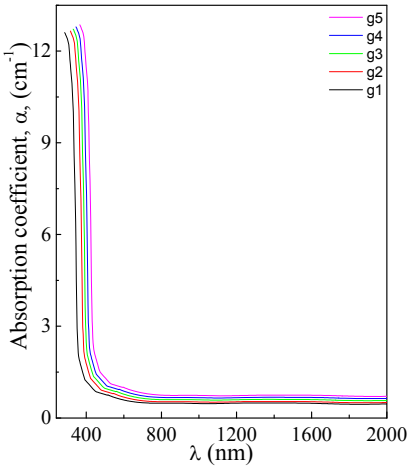

Fig. 2. The absorption coefficient of the glass system $Na_2O - B_2O_3 - TiO_2$ as a function of the wavelength

Table 2. The density (ρ), the activation energy for glass transition (E_t), the optical band gap (E_g), single-oscillator energy (E_0), the dispersion energy (E_d), the third-order non-linear optical susceptibility ($\chi^{(3)}$), the bulk modulus (K) and the optical dielectric constants of the glass system $Na_2O - B_2O_3 - TiO_2$.

Glass	ρ	E_t	E_g	E_0	Ed	χ	K1	K2	n(0)	ε_∞	$\chi^{(3)}$	n_2	α_{e1}	α_{e2}	α_{e3}	α_{e4}
	Kg m^{-3} ±25	Kcal. mol^{-1}		eV			GPa ±0.15				10^{-13}esu	10^{-12}esu		A^3		
g1	2280	98.11	3.34	3.64	9.35	0.895	96.06	93.29	1.89	3.51	1.59	1.98	7.217	7.466	7.215	5.362
g2	2330	103.16	3.21	3.49	9.47	0.860	94.85	91.49	1.93	4.01	3.28	3.95	7.176	7.461	7.174	5.780
g3	2370	107.84	3.05	3.28	9.80	0.817	93.30	89.26	1.99	4.61	6.81	7.68	7.192	7.513	7.191	6.221
g4	2420	113.35	2.96	3.18	10.51	0.793	92.40	88.01	2.07	5.64	18.56	19.96	7.139	7.471	7.138	6.772
g5	2490	117.95	2.85	3.06	11.12	0.764	91.25	86.49	2.15	6.48	36.23	38.73	7.047	7.387	7.046	7.048

The theoretically calculated optical mobility gap, E_g, can be calculated by plotting $\sqrt{\alpha\hbar\omega}$ versus$\hbar\omega$. The E_g value was then calculated from a linear extrapolation to zero ordinate. It was found that the E_g values decreases with increasing TiO_2 content [Table 2]. This behavior is a direct result of the observed shift in the absorption coefficient towards the long wavelength side with increasing TiO_2 content.

The index of refraction has been determined based on only transmittance spectra through the following expression [18-19]:

$$n = (1 + (1 - T^2)^{0.5})/T \quad (2)$$

Glasses based metallic oxides like TiO_2 have relatively high values of the refractive index as in the present study. Fig. 4 represents the index of refraction (n) for g1-g5 glasses as a function of wavelength. It was noted that, the n values are directly proportional to the incident photon energy and in contrary increases with the increasing TiO_2 content. In sodium borate glasses, Ti^{6+} ions would create non-bridging oxygens (NBO) by breaking the B–O–B network and result in converting some of BO_4 into BO_3 units. TiO_6 and TiO_4 units of TiO_2 are distributed along with BO_3 and BO_4 structural units in network randomly. The NBOs are charge balanced by Ti^{6+} ions, BO_4 and BO_3 units in a random three dimensional network configuration which increase the coordination number of the glass [7, 20].

Consequently, the average coordination number of the studied glasses increases, which further increases the refractive index. The creation of NBOs creates more ionic bonds, which results in larger polarizability of ionic bonds over the mostly covalent bonds of bridging oxygen [22].

As shown in Fig. 3, the refractive index, n, decreases with increasing the wavelength of the incident photon, while at higher wavelengths the refractive index, n, tends to be constant for all compositions under study. Here the values of refractive index for all compositions can be fitted according to the Wemple–DiDomenico (WDD) dispersion relationship [23];

$$\frac{1}{n^2(h\nu)-1} = \frac{E_0}{E_d} - \frac{(h\nu)^2}{E_0 E_d} \quad (3)$$

where E_0 is the single-oscillator energy and E_d is the dispersion energy or single-oscillator strength where the refractive index factor $(n^2-1)^{-1}$ can be plotted as a function of $(h\nu)^2$. By using a linear fit of the previous relation as shown in Fig. 4, the values of the E_0 and E_d can be determined from the intercept and the slope.

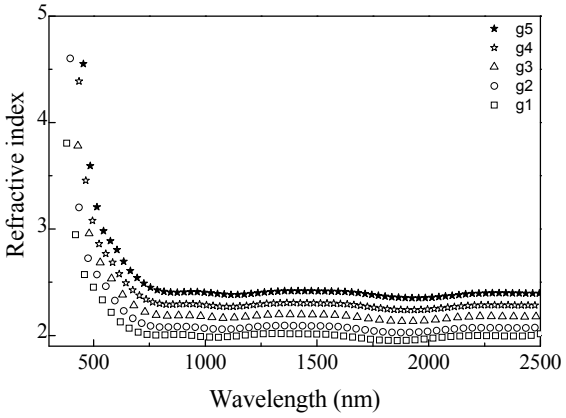

Fig. 3. The refractive index of the glass system $Na_2O - B_2O_3 - TiO_2$ as a function of the wavelength. Solid lines are Cauchy's fitting according to $(n = a + (b/\lambda^2))$

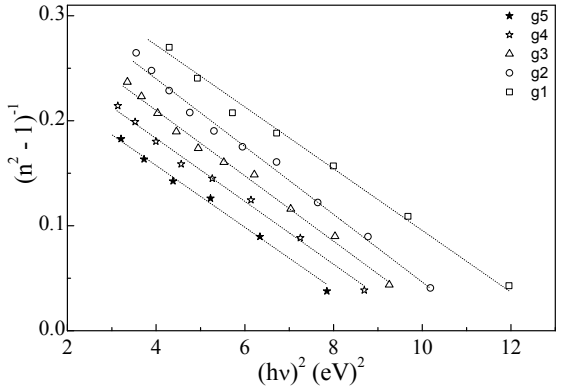

Fig. 4. Plots of refractive index factor $(n^2-1)^{-1}$ vs. $(h\nu)^2$ for the glass system $Na_2O - B_2O_3 - TiO_2$

More understanding of the behavior of the refractive index of the investigated glasses can be obtained through the variation of the value of E_d. As listed in Table 2, it is clearly seen that the values of E_d increase with increasing the TiO_2 concentration. This increase is mainly attributed the higher coordination number (6) of TiO_6 compared to that of BO_4 or BO_3 structural units of B_2O_3 [24-25]. The variation of the static refractive index n(0) as a function of TiO_2 concentration is obtained by letting the frequency of the photon energy tends to zero ($\nu \rightarrow 0$), from Eq. (3), the static refractive index is given by $n_0 = \sqrt{1+(E_d/E_0)}$. The obtained values of E_0, E_d, and n(0) are listed in Table 2. It was observed that the single-oscillator energy E_0 decreases while both the dispersion energy E_d and $n(0)$ increase with the increase of TiO_2 content. The bevaiour of the static refractive index of TiO2 prepared with nano-spin coating in the form of a film is similar to that obtained in this study [26].

From the W–D model parameters (E_0, E_d) and using a generalized Miller's rule in the limit $\nu \rightarrow 0$, the third-order nonlinear optical susceptibility ($\chi^{(3)}$) can be estimated [27]:

$$\chi^{(3)} = 4.02 \times 10^{-15} \quad (E_d / E_0)^4 \qquad esu, \qquad (4)$$

Compared with the values of $\chi^{(3)}$of other glasses [21], the estimated values of $\chi^{(3)}$, as listed in Table 2, are rather large, indicating that the glasses under study are interesting materials for nonlinear optical devices. Values of $\chi^{(3)}$ have been found to increase with increasing TiO_2 content, thus, the nonlinear index of refraction can be determined through the following equation [27-28]:

$$n_2 = \frac{12\,\pi\chi^{(3)}}{n} \qquad (5)$$

The n_2 values have been plotted versus λ for g1-g5 glasses. The n_2 values are increasing with the addition of TiO_2 at the expense of B_2O_3. This behavior of n_2 can be correlated to the optical band gap through this relation $n_2 \propto (E_g)^{-4}$ [27]. According to which, n_2 values are inversely proportional to the fourth order of the E_g values. This showed that the results are consistent with the given relation. Similar behaviour for n_2 has been observed for other materials such as pure silica ($8.1 \pm 1.2\ 9\times10^{-14}$ esu) and As_2S_3 ($3.51\ 9\ 10^{-11}$esu) at 800 nm. These results clearly indicate that the calculated values of n_2 for the glasses under study are large in comparison with the reported values [28-29]. Glasses with high n_2 values need moderate laser pulses to change their refractive index. Therefore, the present glasses may be explored for application in fast optical switching devices. Moreover, the high-n_2 materials exploiting third-order electronic polarization may have short response time and compact fiber design, which may further boost their application in high-speed signal communication as reported by Kreidl [30].

It is worth mentioned that, the total optical electronegativity difference, $\Delta\chi$, for ternary glasses can be estimated by substituting the value of the band gap, E_g, into Dufy's equation [6]:

$$\Delta\chi = 0.2688\, E_g, \qquad (6)$$

Based on the values of the optical electronegativity, the bulk modulus can be estimated using the following relationship [31-32]

$$K1 = 168.58 + 30.3 \ln(0.102\ \Delta\chi). \qquad (7)$$

Aly [31] concluded that, the bulk modulus can be estimated based only on the E_g value through the following relation:

$$K2 = 13.89\ E_g + 46.9 \qquad (8)$$

The deduced values of K based on optical electronegativity or E_g values are listed in Table 2 as K1 and K2 respectively. The K1 and K2 values are in good agreement with each others. Then the electronic polarizability (αe) for the glasses has been calculated based on the K_1, K_2 and E_g values as well as detailed here [31] and listed in table 2 as αe_1, αe_2 and αe_3 respectively. The observed values of αe are found in good agreement with each others.

Theoretical determination of the elastic moduli of oxide glasses has been studied before in terms of several models, two of them are Makishima-Mackenzie model [33] and bond compression model [34]. In the two models, the computed elastic moduli differ to some extent from the determined experimentally elastic moduli [35]. Moreover, the computed elastic moduli via the optical properties are comparable to those determine from experimental techniques. The difference between the theoretical and experimental determined elastic moduli of oxide glasses may be due to the ignorance of some parameters such as the interaction between oxygen atoms and different cations, their coordination number and decisive bond lengths between the different structural units constitute the glass matrix. Thus, the values of the estimated bulk modulus of the studied glasses are larger than that experimentally determined of borate glasses had a comparable composition [21, 36].

On the other hand, the variation of T_g with TiO_2 content and heating rate for the studied glasses is shown in Fig. 5. There is an observed increase in T_g values as the TiO_2 content increased from 0 to 5wt. %. Also, Fig. 5 shows that the T_g values increases with increasing the heating rate. The results of Fig.5 were fitted according to the empirical relationship [37]

$$T_g = \partial + \Delta \ln(\emptyset) \qquad (9)$$

where ∂ and Δ are constants for a given glass composition. Eq.9 with ∂ and Δ values for 80 B_2O_3 – 20 Na_2O (wt %) – x TiO_2(x= 0, 0.5, 1, 3 and 5 gm) glasses are shown on the same figure. The activation energy for glass transition E_t has been evaluated using the so-called Kissinger's formula [38]. For homogeneous crystallization with spherical nuclei, it has been shown [39] that the dependence of T_g on ∅ is given by:

$$ln(T_g^2/\emptyset) = E_t/RT_g \ + const. \qquad (10)$$

where R is the universal gas constant. Plots of $ln(T_g^2/\emptyset)$ versus$10^3/T_g$ for these glasses indicated linearity for all the heating rates as shown in Fig. 6. The values of E_t are found to increase with the increase in TiO_2 content (see Table 2).

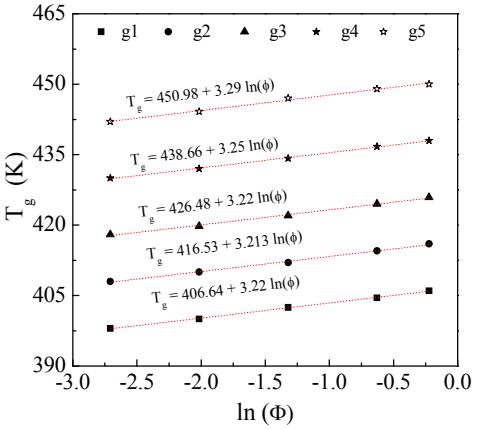

Fig. 5. The plots of T_g vs. $ln(\phi)$ for $Na_2O - B_2O_3 - TiO_2$ glasses

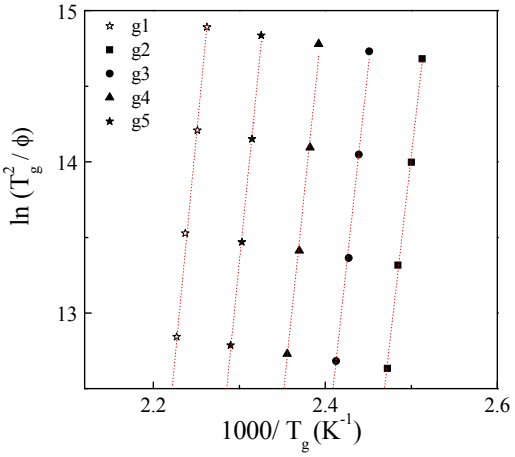

Fig. 6. The plots of $\ln(T_g^2/\phi)$ versus $1000/T_g$ for $Na_2O - B_2O_3 - TiO_2$ glasses

The above results can also be discussed on the basis of a parameter called fragility (F), which characterizes and quantifies the anomalous non-Arrhenius transport behavior of glassy materials near the ergodicity breaking glass transition region [40 - 41]. Fragile glasses are substances with non-directional interatomic/intermolecular bonds. Strong glasses are those which show resistance to structural degradation and usually associated with a small ΔC_p. Fragility (F) is calculated by using the following relation [42]

$$F = \frac{E_g}{T_g.R.\ln(1.01)} \qquad (11)$$

The value of (F) is found to decrease with the increase of TiO_2 content. This behavior indicates that the glasses become more fragile and their tendency to structural rearrangement increases with increasing non-directional interatomic bonds. The obtained values of the fragility index for the studied glasses at different heating rates and TiO_2 content are shown in Fig.7. These values agree well with a work by Sipp et al. [43] on the relaxation kinetics of borosilicate melts.

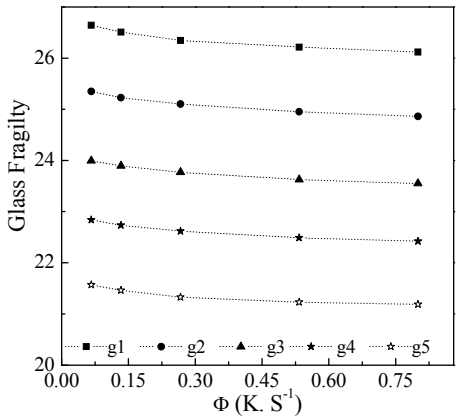

Fig. 7. The glass fragility versus the rate of heating (ϕ) for $Na_2O - B_2O_3 - TiO_2$ glasses

Studying of structural relaxation in the glass transition region of glass-forming liquids has great attention from both academic and technological points of view. Structural relaxation processes in glasses occur at temperatures less than their T_g. Glass forming liquids is defined as fragile glass former exhibiting a non-Arrhenius temperature dependence of the viscosity while that exhibiting Arrhenius behavior is known as strong glass formers [38-39]. Fragile glasses have higher ionic bond character as compared to the covalent bond component. The limit for kinetically fragile-glass-forming (KF) liquids is characterized by a high value of F (F≈200) [44] while the limit for kinetically strong glass-forming (KS) liquids is reached for a low value of F (F≈16) [28-29]. Strong glasses that show resistance to structural degradation in the liquid state. For 80 B_2O_3 – 20 Na_2O (wt %) – x TiO_2 (x= 0, 0.5, 1, 3 and 5 gm) glasses the values of F are near to KF limit (Fig.7). This indicates that all the glasses in the present study are obtained from KF liquids. Hence the stable glass with higher GFA requires less activation energy for the glass transition process [45]. The fragility behavior of the studied glasses is in a good agreement with the decrease of the bulk modulus and the optical band gap.

4. Conclusions

In this study, it was found that as the TiO_2 content increased, the glass transmittance decreases while the absorption increases. This behavior may be due to the replacement of B_2O_3 with density and molecular weight less than that of TiO_2. The optical mobility gap, E_g, decreases with increasing TiO_2 content which as a direct result of the observed shift in the absorption coefficient towards the long wavelength side with increasing TiO_2 content. It was noted that, the index of refraction values are directly proportional to the incident photon energy and in contrary increases with the increasing of TiO_2 content. Introducing TiO_2 in the glass network resulted in an increase in coordination number of the glass, so the concentration of its basic structural unit TiO_6 units will

increase resulting in the creation of more NBOs. Consequently, the average coordination number of the studied glasses increases, which further increases the refractive index.

The values of the third-order nonlinear optical susceptibility ($\chi^{(3)}$) were found to increase with increasing TiO_2 content which can be correlated to the optical band gap through the relation $n_2 \propto (E_g)^{-4}$.

Based on the values of the optical electronegativity and the optical band gap, the bulk modulus (K) can be estimated. The values of the two parameters are in good agreement with each others. The decreasing behavior of the bulk modulus can be related to the decrease of T_g and the increase of the fragility of the glasses with increasing TiO_2 content.

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