Optical Properties of TeO_2 TiO_2 B_2O_3 Glass System

Ghada Adel

Physics Department, Faculty of Science, Al-Azhar University (girls branch), Nasr City, Cairo, Egypt.
ghadahelmy@outlook.com

The optical properties of glasses having a composition $60TeO_2$ x TiO_2 (40-x) B_2O_3, where (x = 10, 20, 30) have been studied. It was found that the values of the optical energy gap decrease by increasing TiO_2 content. The optical electronegativity has been calculated from the optical energy gap. It was found that all samples are considered to be covalent in nature. Refractive index, optical basicity and the polarizability of oxide ions have been calculated from optical electronegativity. The glasses are found to possess a high refractive index (2.764 – 2.807), a comparatively narrow band gap (1.76 eV – 1.66 eV), high oxide ion polarizability (3.074 $Å^3$ – 3.099$Å^3$) and high optical basicity (1.464 - 1.477) and small single bond strengths (350.9 – 312.3 kJ mol^{-1}). Finally, all the prepared samples have higher values of third order nonlinear susceptibility (7.810-8.99) $x10^{-12}$ esu, which indicates that all samples are promising materials for nonlinear optical devices.

1. Introduction

Nonlinear optical materials provide the backbone of optical signal processing. Practical applications of these materials include efficient switching, image processing, and use in various electro-optic devices [1]. The optical energy gap and the refractive index are the most exciting and essential properties of glass materials. The calculation of the refractive index is very imperative to determine the suitability of glass material to be optical devices [2]. Glasses with higher refractive indices are expected to have higher third order nonlinear susceptibility values [3].The understanding of optical basicity would be useful for the design of the novel optical functional materials with higher optical performances [3]. The optical electronegativity is one of the most significant parameters in understanding the nature of chemical bonding and many transport physical parameters can be expected by using it [4]. Also, the polarizability is correlated to many physical and chemical properties such as optical basicity, electro-optical effect, dielectric properties and chemical stability along with optical nonlinearity [4]. Polarizability is one of the most important properties which govern the nonlinearity response of the material [3]. Many works [5-9] reported that telluride glasses have high optical nonlinearity and have practical application as nonlinear optical materials. Borate glasses have been given attention due to their practical applications in the fields of linear and nonlinear optics and related techniques [10]. ($B_2O_3TeO_2$) glasses have

been shown advanced changes in both the boron and tellurium coordination with the addition of other ions [6, 11]. Glasses with high TiO_2 content are of great interest in basic research and technological applications because of their optical properties and good chemical resistance [12, 13]. The aim of the present work is to study the optical properties of $60TeO_2$ x TiO_2 (40-x) B_2O_3 glasses, where (x=10, 20, 30) and make correlation between polarizability of oxide ions, optical basicity, refractive index, and nature of bonding of the studied glasses.

2. Experimental

Glasses having a composition $60TeO_2$ $xTiO_2$ (40-x) B_2O_3, where (x = 10, 20, 30) were prepared by the conventional melt quench technique. Raw materials have employed: TeO_2 (STREM Chemical, USA 99%), TiO_2 (Sherwood Medical USA, 99.99%), B_2O_3 (STREM Chemical, USA 99.9%). Proper weights of TeO_2, TiO_2 and B_2O_3 in accurate molar ratio were mixed to obtain uniform acceptable fine powder and then, placed in a porcelain crucible and heated in an electric furnace whose temperature was elevated in steps to 1100^0C for half an hour. Then, the molten samples were rapidly cooled to room temperature by pouring it onto a cooper plate and successively pressing it with another to gain glasses. The studied samples have been characterized by the X-ray diffraction (XRD). All the samples reveal non-crystalline nature as no noticeable peaks were detected in (XRD) spectra. The transmission spectra were measured for all samples of equal thickness (1.8 ±0.2 mm) by using a computerized recording spectrophotometer (type Jasco, V-570).

3. Discussion and results:

3.1 Optical energy gap:

Figure (1) shows the optical transmission spectra for all the studied samples. The absorption edge is observed for all investigated samples. All samples follow one common pattern where it extends over wide wave length range, confirming the non- crystalline nature. The absorption coefficient α of each sample was calculated using the relation [14].

$$\alpha = (1/d)\ln(I_0/I_t) \quad (1)$$

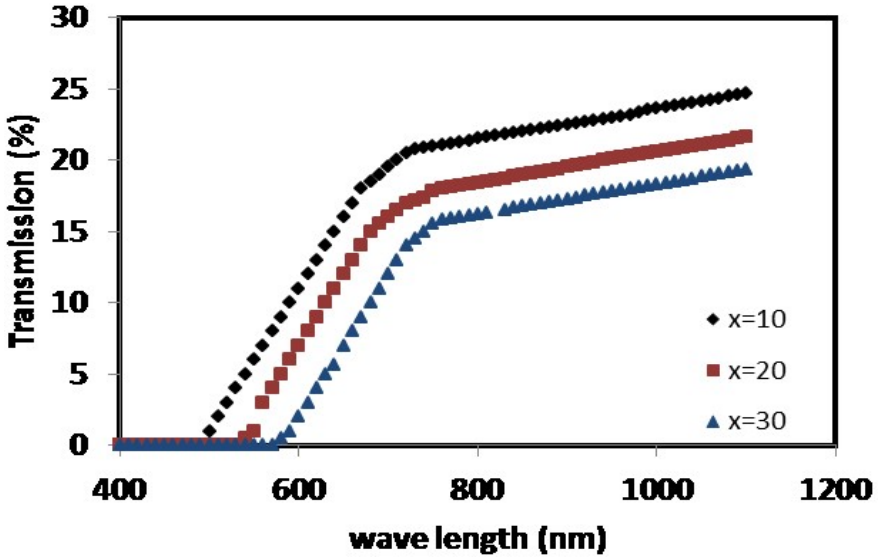
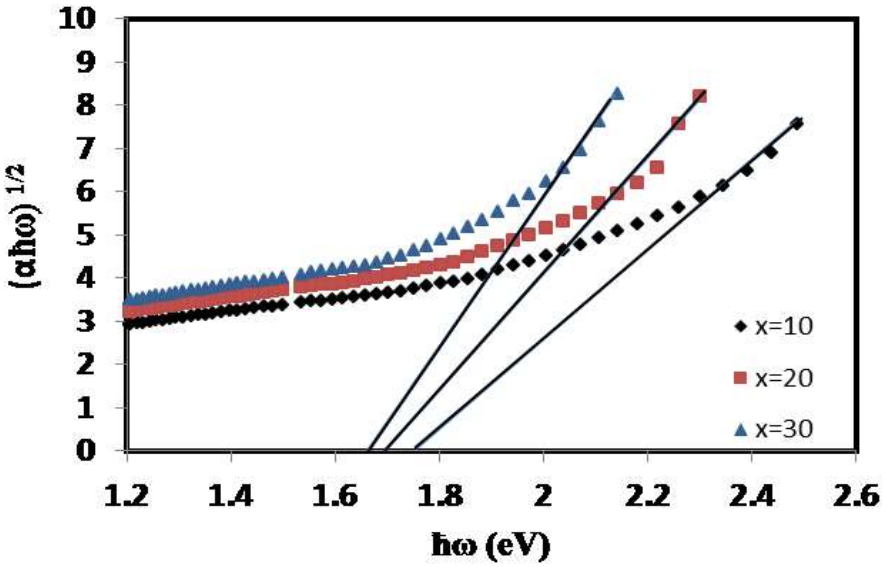


Figure (1): The transmission spectra for all the studied samples.

Where I_0 and I_t are the intensity of the incident and transmitted radiation, respectively and d is the thickness of the sample. Mott & Davis(14) proposed that the relation between the absorption coefficient α(ω) and the photon energy ħω of the incident radiation can be written as follows:

$$\alpha\hbar\omega=\beta(\hbar\omega-E_{opt})^n \quad (2)$$

Where ω is the angular frequency of radiation, β is constant called band parameter, E_{opt} is the optical energy gap and n is a parameter that characterizes the transition process (n=1/2 for a direct allowed transition, n=3/2 for direct forbidden transition, n=2 for indirect allowed transition and n=3 for direct forbidden transition). Plots of $(\alpha\hbar\omega)^{1/2}$, $(\alpha\hbar\omega)^{2}$, $(\alpha\hbar\omega)^{2/3}$ and $(\alpha\hbar\omega)^{1/3}$ versus the photon energy are obtained. Extrapolation of the linear part to the x-axis is well fitted over a wide energy range by n=2. The proposed absorption mechanism is indirect one. This is expected due to the lack of translation symmetry, where the wave vector is not conservative i.e not good quantum number. The values of E_{opt} corresponding to the energy separation between extended states in the valence and conduction band are defined as the intersection between $(\alpha\hbar\omega)^{1/2}$ and ħω as shown in Figure (2).The obtained values of E_{opt} for all the studied glasses are given in Table [1]. It is clear that, the value of optical band gap energy decrease by increasing TiO_2 content. As a result of the replacement of B_2O_3 with TiO_2, the structural changes take place inside the glass. As TiO_2 in the glass matrix increases, B-O-Te is replaced with Ti-O-Te. These structural changes will result in shifting the valence band maximum to higher energies, thus reducing the band gap of the glass system,



Figure(2): The relation between $(\alpha\hbar\omega)^{1/2}$ and $\hbar\omega$ for all the studied samples.

Table (1): The values of optical energy gap, average single bond strength and optical electronegativity for all the studied samples:

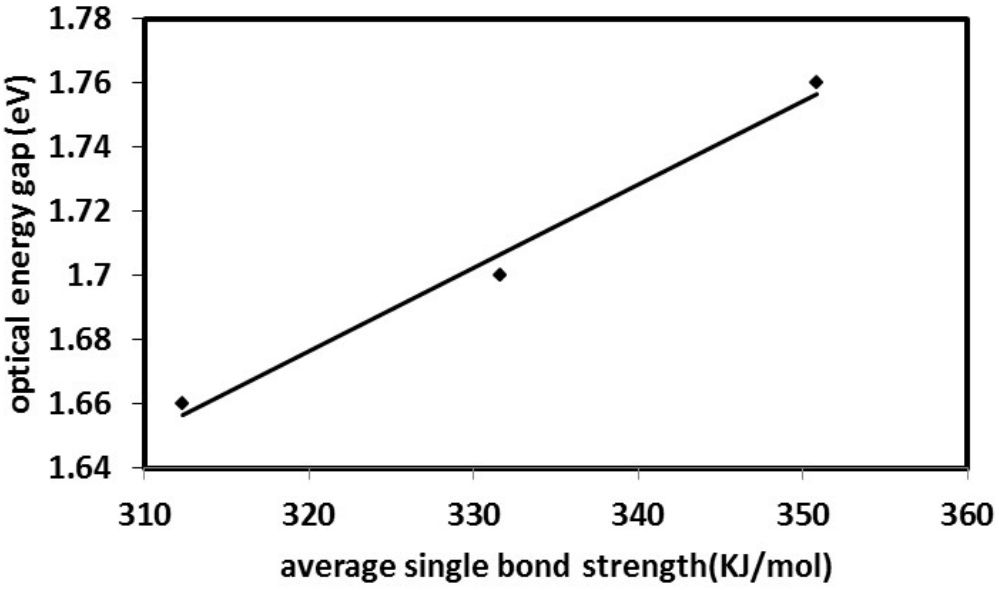
sample	optical energy gap (eV)	average single bond strength (K.J/mol)	Optical electronegativity
$60TeO_2\ 10TiO_2\ 30B_2O_3$	1.76	350.9	0.473
$60TeO_2\ 20TiO_2\ 20B_2O_3$	1.70	331.6	0.457
$60TeO_2\ 30TiO_2\ 10B_2O_3$	1.66	312.3	0.446

3.2. The average single bond strength:

The average single bond strength $B_{M\text{-}O}$ has been determined by the following equation [3].

$$B_{M\text{-}O} = x_{TeO2}B_{Te\text{-}O} + x_{TiO2}B_{Ti\text{-}O} + x_{B2O3}B_{B\text{-}O} \quad (3)$$

where $xTeO_2$, $xTiO_2$and xB_2O_3 are the corresponding portion of the different oxides.The values of the average single bond strength for all the studied samples are listed in table (1). It is clear that the values of average single bond strength decrease by increasing TiO_2 for all the studied samples. Figure (3) represents the dependence of average single bond strength and band gap. The average single bond strength should affect the band gap value; the high bond strength reflects the energy needed for electron liberation i.e the band gap. Figure (3) shows linear dependence which needs more investigation. It was found that optical energy gap decrease by decreasing average single bond strength for all samples. This can be accounted for by considering the bond strength of Ti-O which is lower than other bonds.



Figure(3): The relation between average single bond strength and optical energy gap for all samples.

3.3 The optical electonegativity:

The optical electronegativity ($\Delta\chi^*$) has an extensive possibility in expecting many physical properties of optical materials. The magnitude of optical electronegativity specifies the nature of bonding in the material. The optical electronegativity can be calculated for binary oxide glasses [4] and also, used for ternary oxide glasses [15] from optical energy gap as follows,

$$\Delta\chi^* = 0.2688 \times E_{opt} \quad (4)$$

The values of optical electronegativity are listed in table (1). It was found that the optical electronegativity decrease by increasing TiO_2 content, which indicates that all samples are covalent in nature [4].

3.4. The optical basicity:

The optical basicity has been shown to be a suitable parameter for associating and expecting properties of oxide systems covering a wide range of requests. The high optical basicity means high electron donating power of the oxygen in the oxide glass. The optical basicity can be calculated [4, 15] from the optical electronegativity as follows,

$$\text{Optical basicity} = -0.5\ \Delta\chi^* + 1.7 \quad (5)$$

The values of optical basicity are listed in table (2). It was found that the values of optical basicity increase by increasing TiO_2 content, which means that the studied glasses become more basic.

3.5. Polarizability of oxide ions:

The polarizability of oxide ions can also, be calculated [4, 15] from the optical electronegativity as follows,

$$\text{polarizability of oxide ion} = -0.9\ \Delta\chi^* + 3.5 \quad (6)$$

From Table (2), it was found that, by increasing TiO_2, the values of the polarizability of oxide ions increase which indicates that the glasses become more polarized.

Table (2): The values of optical basicity, polarizability of oxide ions, refractive index, third order nonlinear susceptibility and metallization for all the studied samples:

Sample	optical basicity	polarizability of oxide ions	Refractive index	Third order nonlinear susceptibility (e.s.u)	Metallization
$60TeO_2 10TiO_2 30B_2O_3$	1.464	3.074	2.764	7.810×10^{-12}	0.297
$60TeO_2 20TiO 220B_2O_3$	1.472	3.089	2.789	8.484×10^{-12}	0.292
$60TeO_2 30TiO_2 10B_2O_3$	1.477	3.099	2.807	8.999×10^{-12}	0.288

3.6. The refractive index:

The refractive index is one of the important properties of materials because it is closely depended on the polarizability of oxide ions and local field inside the material[4] .The refractive index also, can be calculated[4,15] from the optical electronegativity as follows,

$$n = -0.73 \ln (0.102\ \Delta\chi^*) + 0.5511 \quad (7)$$

As shown in table (2), the refractive index increase by increasing TiO_2 content. The values of refractive index increase because the values of polarizability of oxide ions increase by increasing TiO_2 content for all the studied samples.

3.7. Metallization criterion of the glasses:

Dimitrov and Sakka [3] calculated metallization criterion for various simple oxides and found that oxides with large refractive index and small energy gap have small metallization criterion .

$$\text{The metallization criterion} = [E_{opt}/20]^{1/2} \quad (8)$$

The values of metallization criterion for all the studied samples are listed in table (2). It was found that the metallization criterion values of the present glasses are found to be less than one and thus all the studied samples exhibit insulating behavior [3] . It was found that the values of metallization decrease by increasing TiO_2 because the values of optical energy gap decrease for all the studied samples.

3.8. Third order nonlinear susceptibility:

The glasses with higher nonlinear optical properties, especially third order nonlinear susceptibility, are desirable to develop nonlinear waveguide devices applicable to optical signal processing [16]. The third order nonlinear susceptibility $\chi^{(3)}$ in esu units was calculated from the values of the refractive index by the following relation [17],

$$\chi^{(3)} = ((n^2-1)/ 4\pi)^4 \times 10^{-10} \quad (9)$$

It was found that the values of third order nonlinear susceptibility which are listed in Table (2) are higher than that of pure silica glass (2.8×10^{-14} e.s.u), which means that all the studied samples are perhaps excellent applicants for nonlinear optical applications [3].

Conclusion:

We try in the present work to get in possible information that can be obtained to clarify the physical behavior of the given system.TeO_2 TiO_2 B_2O_3 glasses are investigated in respect to their refractive index, band gap, oxide ion polarizability, optical basicity, single bond strength and third order nonlinear optical susceptibility. It is found that the glasses possess a high refractive index (2.764 - 2.807), a narrow band gap (1.76 –1.66 eV), a high oxide ion polarizability (3.074– 3.099 Å3), a high optical basicity (1.464 – 1.477), a small single bond strength (350.9 – 312.3 kJ mol^{-1}) and a large third order nonlinear optical susceptibility (7.810 – 8.999)$\times10^{-12}$ esu. On the basis of this study it is suggested that TeO_2 TiO_2 B_2O_3 glasses would be promising materials for nonlinear optics because of their high third order nonlinear optical susceptibility. Such glasses have to be searched among those of high refractive indices, small energy gaps, and small single bond strengths.

References:

1. J .A. Miragliotta , *Applied Research*, **16**, 348 (1995).
2. M.N. Azlan, M.K. Hlimah, S.Z. Shafinas and W.M. Daud, *Chalcogenide letters*, **11**, 319 (2014).
3. V. Dimitrov and T. Komatsu, *J. of University of Chemical Techology and Metallurgy*, **43**, 219 (2010).
4. X. Zhao, X. Wang, Lin, Z. Wang, *Physica*, B,**403**, 2450 (2008).
5. S.H. Farhan, Study of some physical and optical properties of Bi_2O_3 TeO_2 V_2O_5 glasses, Australian J. of Applied Science, 11(2017)171-178.
6. R. El Mallawany, Tellurite glasses hand book- physical properties and data of CRC press , 2001.
7. N. Cupta, A. kaur, A. Khanna, F.Gonzalez, C.Resquera, R. Iordanovo, B.Chen, *J. of Non Crystalline Solids*, **470**, 168 (2017).
8. S.H. Elazomi, H. A.A. Sidek, yyY.S. Rammach, K.A. Matori, M.H.M. Zaid, *Results in Physics*, **8**, 16 (2018).
9. J.Jackson, C. Smith, J. Massera, C. Rivero, C. Bungay, L. Petit, K. Richardson, *Optical Express*, **17**, 9071 (2009).
10. D.Ehrt, Glass Technlogy, **41**, 182 (2000).
11. K. J. Singh, S. Kaur and R. S. Kaundal, *Radiation Physics and Chemistry*, **96**, 153 (2014).
12. C. Jijian, C. Wei, *J. of Non Crystalline Solids*, **80**, 135 (1986) .
13. K. Terashima, T. Uchino, T. Hashimota, T. Yoko, *J. of the Ceramic Society*, **105**, 288 (1997).
14. N.F. Mott and E.A. Davis, "Electronic processes iChemistryn nor crystalline materials", 2nd ed., clarendon press, Oxford, (1979).
15. H,Saudi, Gh Adel, Physical and optical properties of CeO_2 BaO B_2O_3 glasses, *Optics*, **6**, 17 (2017).
16. T. Tashva, V. Dimitrov, *J. of Chem. Tech. and Metallargy*, **52**, 369 (2017).
17. C.C.Wang, *Phys. Rev*. B, **2**, 2045 (1970).