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COMPARATIVE STUDIES OF BISMUTH AND BARIUM BORO-TELLURITE GLASS SYSTEM: STRUCTURAL AND OPTICAL PROPERTIES

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This paper aims to compare the structural and optical properties of ternary Boro-tellurite glass with the addition of two different chemical modifier. Six glass samples from composition $[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{1-x}(BaO)_x$ (x = 0.10, 0.20 and 0.30 mol%) and $[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{1-x}(Bi_2O_3)_x$ (x = 0.10, 0.20 and 0.30 mol%) were prepared by melt quenching method with suitable melting and quenching temperature. The X-ray diffraction (XRD) pattern confirms the amorphous nature of all glasses and the Fourier transform infrared spectroscopy (FTIR) spectra explore the fundamental groups and the local structural units in two different boro-tellurite glasses. The density for both glass series increased as barium oxide and bismuth oxide content increased. The optical band gap, E_{opt} values for bismuth-boro-tellurite glasses are between 2.15–2.4 eV, while barium-boro-tellurite glasses are between 2.25–2.44 eV. The highest concentration of Bi_2O_3 in glass system shows the smallest E_{opt}. In conclusion, the obtained results shows that the addition of bismuth oxide in boro-tellurite glass improves its structural and optical properties.

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Keywords: Barium; Bismuth; Boro-tellurite; Structural; Optical properties

1. Introduction

Boro-tellurite (B_2O_3-TeO_2) glasses have been widely studied because of the unique physical properties of tellurites and its industrial importance in making glasses with desirable structural and optical properties. Since both B_2O_3 and TeO_2 are present in boro-tellurite glasses, it leads to complex specification in the glass structure and optical properties [1]. Therefore, chemical modifiers such as Bi_2O and BaO are added to the glasses to increase its density and to improve its structural and optical properties.

Bismuth is quite unique material among the heavy metals and it can be considered as harmless, non-toxic and non-carcinogenic material. It is valuable in electronics application, ceramic production and good element for "warm" superconductors because of the high polarizability of Bi^{3+} cations. Previous research reported that silicate and borate glasses contained bismuth (III) oxide demonstrate good radiation shielding properties which can be used as radiation shielding material [2–4]. Bismuth borate glass is of great interest in optoelectronic devices due to its low melting temperature (600–800 ^oC), extensive glass formation range, high refractive index ranging from 1.9 to 2.3, high physical and chemical stability, and nonlinear optical property. Another heavy metal which is also harmless is barium which has been used as component of high

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temperature conductors (YBCO) and electroceramics. Barium is not carcinogenic, non poison and it does not bio–accumulate. It is very useful in glass making industries and can increase the refractive index and luster of the glass. Report by Singh *et al.* [13] showed that barium-borate glasses have good value in mass attenuation coefficient and effective atomic number which make good radiation shielding materials.

The study on absorption spectra of solids provides essential information about the band structure and the energy gap. The framework of B_2O_3-TeO_2 glasses is build-up of BO_4 tetrahedral units, BO_3 trigonal units, TeO_4 trigonal bipyramidal, TeO_3 pyramidal and unintentionally at a high B_2O_3 content of TeO_6 octahedral [1,5]. The band gap energy, E_{opt} value for these glasses are between 2.93–3.22 eV. Studies on these glasses have also shown progressive changes in both the boron and tellurium coordination with the addition of other ions. The optical properties of glass Pb-B_2O_3-TeO_2 with different concentration have been studied by Iskandar *et al.* [8].

The aims of this research are: (i) to explore the structural changes of B_2O_3-TeO_2 glasses by adding BaO and Bi_2O_3 using XRD and FTIR spectrum, (ii) to compare the density and molar volume of these two different glass system and (iii) to determine the band gap values through UV-Visible absorption spectra.

2. Experimental Section

The glass system of $[(TeO_2)_{0.7}\ (B_2O_3)_{0.3}]_{1-x}\ (Bi_2O_3)_x$ (x = 0.1, 0.2 and 0.3 mol%) and $[(TeO_2)_{0.7}\ (B_2O_3)_{0.3}]_{1-x}\ (BaO)_x$ (x = 0.1, 0.2 and 0.3 mol%) were prepared by using a melt quenching method. The raw materials of tellurium (IV) dioxide TeO_2, boron oxide B_2O_3, barium oxide BaO and bismuth oxide Bi_2O_3 from Assay, Alfa Aesar were used to prepare for the two glass systems. Each batch of composition was mixed together by using a mortar and pestle for about 20 minutes. Then, the mixture was transferred into an alumina crucible which was put into a furnace set at 350 °C for a period of 30 minutes. Next, the sample was placed again on a different furnace for melting process at 900 °C for about 2 hours. When the melting process was completed, the molten glass was poured into a stainless steel cylindrical shape mould which was preheated at 400 °C for 30 minutes. Then, the sample was annealed at 400 °C for 1 hour. When glass samples have obtained room temperature, it was cut into thickness of about 2 mm. Next, the glass samples were polished manually until its surfaces become flat, parallel and smooth.

The glass samples were also prepared in powder form. These powdered glass samples were characterized using x-ray diffraction analysis (XRD) and fourier transform infrared analysis (FTIR) in the range of 200–2000 cm^{-1}. Both of these characterizations were carried out at room temperature.

The glass compositions with six different concentrations are shown in Table 1. The glass density, ρ_g, was determined by Archimedes principle using distilled water as the buoyant medium. The corresponding molar volume, V_m was calculated using the relation,

$$V_m = M_T/\rho_g \tag{1}$$

where M_T is the total molecular weight of the glass system.

Table 1: Glass compositions with six different composition and concentrations

No.	Compositions	Label
1	$[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.9}(BaO)_{0.1}$	Ba1BTe
2	$[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.8}(BaO)_{0.2}$	Ba2BTe
3	$[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.7}(BaO)_{0.3}$	Ba3BTe
4	$[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.9}(Bi_2O_3)_{0.1}$	Bi1BTe
5	$[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.8}(Bi_2O_3)_{0.2}$	Bi2BTe
6	$[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.7}(Bi_2O_3)_{0.3}$	Bi3BTe

The optical absorption of the glass samples were measured using UV-Visible spectroscopy Shidamatsu Model UV-1650PC of wavelength range from 200 nm to 800 nm. Optical absorption coefficient, α, were calculated by using the following equation:

$$\alpha = 2.303(A/d) \tag{2}$$

where A is absorbance and d is thickness of glass sample .

By using optical absorption coefficient from Equation (2), the optical band gap energy, E_{opt} for indirect transition can be determined using following equation which proposed by Mott and Davis (1979):

$$(\alpha\hbar\omega)^{1/2} = B\,(\hbar\omega - E_{opt}) \tag{3}$$

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

3. Results and discussion

3.1. XRD and FTIR analysis

X-ray diffraction (XRD) is a tool to verify the nature of material. Figure 1 shows the diffractograms of the glass samples of one phase in the range of $5° \leq \theta \leq 90°$. It shows a broad peak at the lower Bragg angle, proving structural disorder at long range indicating that all the samples are amorphous.

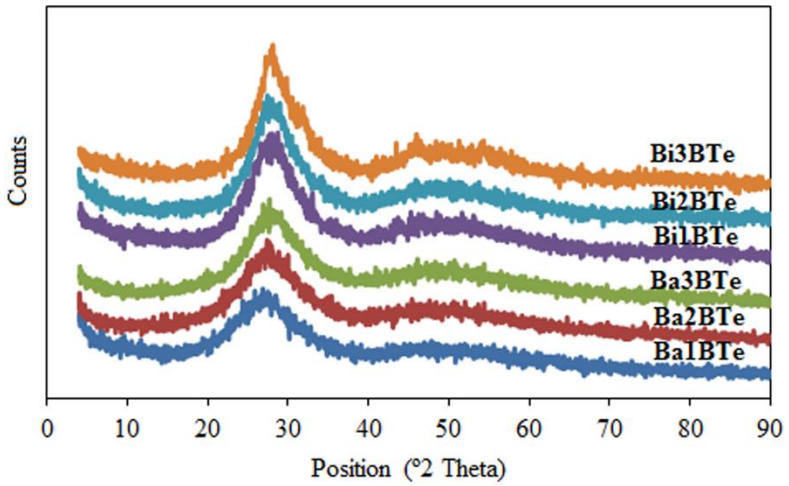

Fig 1. Diffractogram of the $[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{1-x}(Bi_2O_3)_x$ and $[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{1-x}(BaO)_x$ glass systems

Fourier transform infrared spectroscopy (FTIR) is a useful technique which is use to obtain an infrared spectrum of absorption of solid, liquid and gas. It also can provide certain structural clues to the overall molecular structure of material. The infrared spectrums of all boro-tellurite glass system with different additive are shown in Figure 2. These spectrums are between ranges 200–4000 cm^{-1}. From the IR spectra, it shows several peaks which are broad and moderate in band. For $BaO\text{-}B_2O_3\text{-}TeO_2$ glass system, two wide absorption bands in range of 1330–1437 cm^{-1} and 1198–1235 cm^{-1} assigned to stretching vibration of B–O^- in trigonal (BO_3) units from varied types of borate group and B-O stretching vibration in BO_3 units from boroxol rings, respectively. Increasing the BaO content in glass system: (i) creates a new absorption peak at 1015 cm^{-1} which attributed to the vibration of non bridging oxygen in the form of (BO_4) unit [15] (ii) generate the shift of band from ~681 to ~670 cm^{-1} (due to Te-O vibrational in trigonal pyramidal (TeO_3) group) [15]. While absorption peak at ~300 cm^{-1} indicates the presence of BaO.

The IR spectra for $Bi_2O_3\text{-}B_2O_3\text{-}TeO_2$ glass system show same trend with $BaO\text{-}B_2O_3\text{-}TeO_2$ glass system at absorption band range at 1198–1437 cm^{-1}. The intensity of these absorption bands are slightly changed maybe due to the increase of Bi_2O_3 content which increase the non bridging oxygen (which also supports our result discussions in optical properties). The peak region at 1018 cm^{-1} attributed to the absorption vibration of BO_4 unit. Although, this peak vanish when Bi_2O_3 content are increased. The absorption band at range 860–912 cm^{-1} attribute to Te-O bending vibration in TeO_3 unit. Increase of Bi_2O_3 content generates the shift of absorption band from ~612 to ~600cm^{-1} (assigned to Te-O bond vibrational in TeO_4) [15]. The absorption bands in the range below 500 cm^{-1} occur due to the oscillations of the Bi-O and Bi-O-Bi in octahedral (BiO_6) [2].

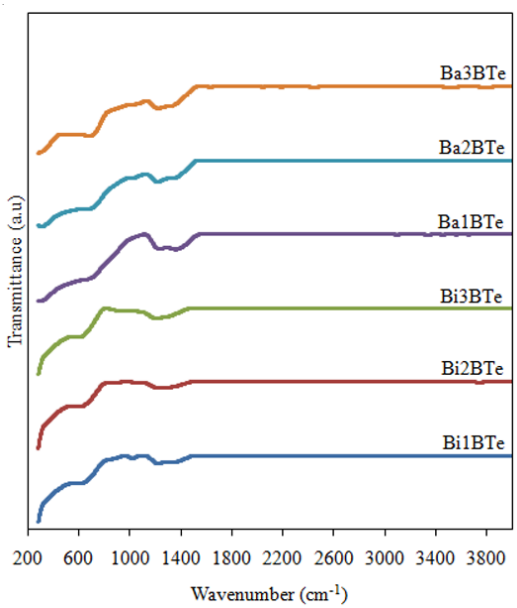

Fig. 2. FTIR spectra of all glass samples

3.2. Density and molar volume

Density of glass is one of the simplest physical properties that can be measured. It can be defined as the degree of compactness of a substance/glass structure. The data obtained for density and molar volume for all glasses are shown in Table 2. The density was measured by Archimedes' method and molar volume was calculated using formula as mention before. Density for both glass systems are increased as BaO and Bi_2O_3 contents increase. It also can be seen that the glasses containing Bi_2O_3 show higher density compare with glass containing BaO. It can be easily explained with the high atomic weight of Bi_2O_3 (465.96 g/mol) compared with TeO_2–B_2O_3 (229.2 g/mol) and BaO (153.3 g/mol). The increase of density for both glass series is because of the replacement of the borotellurite atom with the bismuth and barium atoms. Tuscharoen *et al.* [12]

have report that, from a microscopic perspective, the increase in density of glasses is probably due to increase in the number of non-bridging oxygen (NBO) atoms and may be attributed to replacement of a low–density oxide B_2O_3 (2.46 g/cm^3) and TeO_2 (5.67 g/cm^3) by a high–density oxide Bi_2O_3 (8.99 g/cm^3). The glass density in present study has been compared with previous research as shown in Table 3. It can be seen that Bi_2O_3-B_2O_3-TeO_2 glass system shown high density compared with binary B_2O_3-TeO_2 glass system and also with other glass systems.

The molar volume can be described as the volume occupied by unit mass of the glass samples. Molar volume can be used as a parameter to identify an open structure that is highest value of molar volume corresponds to the maximum open structure [13]. Generally, the density and the molar volume show opposite behaviors, but it does not occur to Bismuth-boro-tellurite glasses. This anomalous behavior was reported by Ooi *et al.* [10] and Halimah *et al.* [7]. The molar volume will be increased whenever the number of space in the network increased. The increase of the molar volume resulted from process of bond breaking which create non-bridging oxygen atom. The bond breaking process occurred with the presence of glass modifier Bi_2O_3 in the glass medium. The increase of the molar volume also can be resulted from an increase in the bond length or an increase in the interatomic space between atoms. In addition, the increasing of Bi_2O_3, produce more structural free volume.

Table 2: Density, molar volume and optical band gap of all glasses

No.	Glass system	Density (g/cm^3)	Molar Volume (cm^3 mol^{-1})	Optical Band Gap, E_{opt} (eV)
1	Ba1BTe	3.38	39.97	2.44
2	Ba2BTe	3.56	38.41	2.29
3	Ba3BTe	3.63	38.20	2.25
4	Bi1BTe	4.81	34.49	2.40
5	Bi2BTe	5.56	35.83	2.35
6	Bi3BTe	6.24	37.31	2.15

Table 3: Density value for present study compared with previous glass system

No.	Glass system	Density (g/cm^3)
1	Bi_2O_3 - B_2O_3 -TeO_2 [present]	4.52 – 6.24
2	BaO- B_2O_3 -TeO_2 – [present]	3.38 – 3.63
3	B_2O_3 - TeO_2 [7]	4.71 – 4.97
4	PbO - B_2O_3 - TeO_2 [8]	4.21 – 5.29
5	BaO - Bi2O3-Borosilicate [9]	3.45 – 4.21
6	BaO/CaO – borate [13]	2.87 – 3.19

3.3 Optical Properties

Absorption spectrum of solids provides important information about the structural properties and the optical band gap energy. Limkitjaroeporn *et al.* [6] reported that analysis of the absorption spectrum in the lower energy part can gives information about the atomic vibrations, while at the higher energy part of spectrum gives information about the electronic state in the atom. Selvaraju *et al.* [15] mentioned in their research paper that when an electromagnetic wave interacts with a valence electron, both direct and indirect optical transitions occur across the

energy gap. However, indirect transitions involve simultaneous interaction with lattice vibrations and the wave vector of the electron.

In present research, the optical band gap energy (indirect transition) of all glasses were obtained from the slope of the extrapolating curves at $(\alpha\hbar\omega)^{1/2} = 0$, as shown in the Figure 3. Optical band gap for all glasses also are presented in Table 2. It can be seen that E_{opt} value is decreased as BaO and Bi_2O_3 content increase. This behavior may be associated with the structural changes in glass network occurring after addition of glass modifier that is BaO and Bi_2O_3. Increasing of modifier concentration generates more of NBO in glass matrix. These leads to a degree of electrons localization and as a result increase in the donor centers in the glass matrix [6]. In binary boro-tellurite glass, non bridging oxygen atoms are already present, and with the addition of Bi_2O_3 as a modifier, increase non bridging oxygen [1]. The band gap energy value of $70TeO_2$-$30B_2O_3$ glass reported by El-Mallawany [1] is 3.22 eV which is found to be high than prepared glasses. The highest concentration of Bi_2O_3 (Bi3BTE) gives smallest value of E_{opt} that is 2.15 eV.

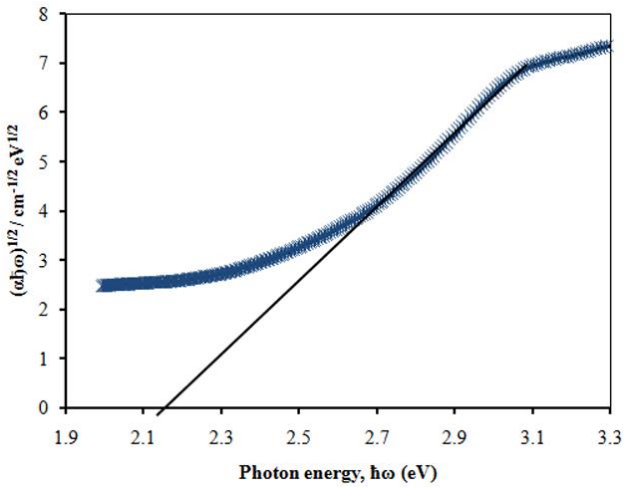

Fig. 3. Plot of $\alpha\hbar\omega$ versus $\hbar\omega$ for indirect transition of Bi3BTe glass.

4. Conclusions

Structural and optical properties of two different glass systems have been studied. The highest density in bismuth-boro-tellurite glass system is ~41.83% bigger than the highest density in barium-boro-tellurite glass system and ~20.35% bigger than boro-tellurite glass [7]. The density of glass system is dependent on the composition which is the higher the compactness of the structure, the higher the density. Optical band gap energy value, E_{opt} was found to be decreased with increase of barium and bismuth concentration, which is due to present of non bridging oxygen in glass matrix. The E_{opt} values for present glasses are less than binary boro-tellurite glass from previous research. Hence, it was found that bismuth oxide Bi_2O_3 can improve structural and optical properties of boro-tellurite glass.

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