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Novel compositions of Bi_2O_3-ZnO-TeO_2 glasses: Structure and hardness analysis

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ABSTRACT

Tellurite based glasses have been prepared with various glass compositions such as yBi_2O_3-xZnO-$(100 - x - y)TeO_2$ glass system (y = 0.2, 1.0, 2.0, 3.0, 4.0, 5.0, and 8.0 mol% ratio and x = 14, 19, 19.8, and 20 mol%). The purpose of the work is to investigate the effect of glass compositions on the structure and hardness under the indentation loading test. Up till now, the experiences of the preparation of tellurite based glasses showed that it has high fragility structure at room temperature compared to boroxide, and chalcogenide-based glass materials. In this study, the thermal, mechanical and structural properties of Bi - based tellurite optical glass materials were investigated at room temperature. Results indicated that increased refractive index ratio of Bi has pronounce effect upon the transition temperature while the hardness value of the lassy material showed a reduction in response to this increased refractive index value of Bi. The obtained results further could be correlated with compositions that effects on the structural changes [for TeO_4 (tbp) to TeO_3 (tb)] having non-binding oxygen (NBO) due to the elastic deformation of Te—O bonding and expansion of interatomic distances when considered the data of the Vickers' hardness, FT-IR, and Raman spectra. Here, it can also be emphasized that obtained the thermal stability, $(T = T_x - T_g)$, of the glass material, decreases from 80 to 37 °C as the melting temperature increases from 800 to 1025 °C, possibly leading to a decrease in microhardness and deformation in the glass materials.

1. Introduction

Tellurite (TeO_2) based oxide glass is one of the potential host materials for industrial applications when doped with rare earth elements or bismuth oxide (Bi_2O_3) contents, especially, as a source fiber laser, fiber amplifier, and optical fiber due to its low melting tem`perature (at around 800 °C), and low phonon energy (600–700 cm^{-1}) when compared with silicate, and borate glasses [1–6]. Besides the advantages of the telluride glasses, there is a lack of mechanical properties like fragility which should be improved to increase the mechanical stability of these materials in contrast to other glassy materials [2]. In addition, Bi_2O_3 based oxide glass materials show some similar tendency with TeO_2 such as thermal stability, high refractive indices, and large optical transmittance from near ultraviolet (N-UV) to mid-infrared (M-IR) region (up to about 7 μm) which has broad band emission in the NIR luminescence from 900 to 2000 nm spectral region might be potential sources for the luminescence based devices [1,2]. Yang et al. emphasized that brittle optical glass materials have four types of crack initiation under the indentation such as; radial crack; lateral crack; median crack; and ring/cone crack [3]. Moreover, Lima et al. also emphasized that the fragility of the glasses comes from vicinity of the glass transition temperature [4]. They observed that glass transition temperature, T_g could be associated with structural changes from TeO_4 trigonal bipyramid (tbp) to TeO_3 trigonal pyramid (tp) containing non-bridging oxygen [4]. In addition, Mohamed et al. showed that the zinc atoms increase strengthen the whole network structure due to its bridging oxygen [5].

Under the normal conditions, it has been known that a pure TeO_2 does not form a glass, and it can be a form of the amorphous structure with certain other oxides like PbF_2, K_2O, Nb_2O_5, Li_2O, ZnO, GeO_2, Bi_2O_3 to obtain high-quality glass materials [6–11]. In literature, there are several publish articles related with glass network cover Bi_2O_3 like PbO-Bi_2O_3-B_2O_3 and PbO-Ga_2O_3-Bi_2O_3 while a few with TeO_2 [1]. For

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example, Gumenyuk et al. stressed that the bismuth is a polyvalent element with four oxidation states such as: Bi^{5+}, Bi^{3+}, Bi^{2+} and Bi^{+} show two processes that one of them is reduction (at a lower valence state), and the other is oxidation (at a higher valence state) affected by the melting temperature, glass compositions, and Bi_2O_3 concentrations [11]. To best of our knowledge, there is little work on the determination of mechanical, and structural properties before technical application as an optical fiber drawing, and ultra-thin glasses. When considered the glass as a solid-like behavior, measurements of the structural and microhardness demonstrates the deformation of the strength of Te—O, and Bi—O chemical bonds under indentation loading. Its means that, upon application of a stress, glass undergoes instantaneous deformation such that the ratio of the stress to the resulting strain which is a constant called as modulus of elasticity or briefly Young's modulus [12]. The determining these parameters give rise to the description and understand the nature of bonding in the solid state of the mechanical properties of the glass materials [12]. Also, understanding of the chemical bonding and structure of the glass samples could be related to observed optical properties of materials such as refractive index and energy band gap [13]. In the meantime, Vickers' hardness of the $15Na_2O$-15ZnO-$70TeO_2$ glasses was measured as a 3 GPa by Watanabe et al. whom observed that TeO_2 based glasses has a high fragility when compared with silicate and borate based glasses [1]. Due to the high fragility properties of the tellurite glasses, the relationship between the glass structure, compositions and temperature needs to be improved by considering such as various glass compositions, melting temperature and preparation environments.

In this study, we have investigated the glass transition temperatures, energy band gaps, refractive indices, hardness, and structural properties of the transparent tellurite glasses as a complementary study on the optical, structural, and mechanical properties of the Bi_2O_3-ZnO-TeO_2 glasses for various glass compositions ZnO and Bi_2O_3. First of all, thermal parameters, such as glass transitions, (T_g), crystallization, (T_c) and melting, (T_m) temperatures were determined using differential scanning calorimetry (DSC). Then, the effect of increased contents of Bi_2O_3 in the glass network on the refractive indices was studied which showed an increasing tendency. The effect of the Bi_2O_3 contents on the glass structure was evaluated by considering the FT-IR, Raman spectra, and X-ray diffractometer (XRD) techniques. Prior to this work synthesized glassy material was well polished, and heat-treated glasses at 300 °C in 6 h. Vickers' hardness values were measured for the glass samples from different points on the surfaces of the glass materials. The Vickers hardness decreases with the increase of Bi_2O_3 contents from 0.334 to 0.304 GPa for the 1.0 to 8.0 mol% Bi_2O_3 glass compositions, respectively. As a result, it might be pointed out that the hardness of the prepared glass materials could be related with glass transition temperature under the Vickers indentation test.

2. Materials and methods

2.1. Preparation of Bi_2O_3-ZnO-TeO_2 compositions

The glass samples were prepared by the conventional melt-quenching technique. Analytically pure reagents Bi_2O_3 (Aladdin, 99.9% purity), ZnO (Aladdin, 99.0% purity), and TeO_2 (Aladdin, 99.99% purity) were selected as raw materials. In the experimental steps, two sets of samples were prepared with 20 and 100 g batch corresponding to the glass compositions in mol% of yBi_2O_3-xZnO-$(100 - x - y)TeO_2$ and were mixed homogenously in an agate mortar, and then melted at 850 °C in a ceramic crucible for 20 min in an air atmosphere. In order to make spectroscopic and hardness measurements, two materials were selected during the synthesize that the 20 g materials for spectroscopic and 100 g materials for the hardness measurements, respectively. The prepared glass samples are given in Table 1. Consequently, the melt was quickly cast onto a stainless steel plate and immediately pressed with another steel plate in order to prevent the glass samples from phase separation and devitrification. All the samples were annealed at 300 °C for 6 h, and then polished for optical measurements.

Table 1
The prepared glass samples at different yBi_2O_3 ratios (yBi_2O_3-xZnO-$(100 - x - y)TeO_2$).

Samples	Bi_2O_3 (mol%)	ZnO (mol%)	TeO_2 (mol%)
B0ZT	0.0	20	80
B02ZT	0.2	19.8	80
B1ZT	1.0	19	80
B1Z1T	1.0	14	85
B2ZT	2.0	19	79
B3ZT	3.0	19	78
B4ZT	4.0	19	77
B5ZT	5.0	19	76
B8ZT	8.0	19	75

2.2. Characterizations

Differential scanning calorimetry (DSC) scans of as-cast glass samples were carried out in a TA Q600 DSC. The DSC scans were recorded with the heating rate of 10 °C/min between 20 and 900 °C temperatures in a platinum crucible. DSC Instrument Universal Analysis Program was used to determine the glass transition temperatures, T_g, selected as the inflection point of the step change of the calorimetric signal, and the crystallization peak temperatures, T_p, were measured as the maxima of the exothermic event. Refractive indices of the glass samples were measured using Metricon Model 2010/M Prism Coupler at 632 nm laser wavelength. Absorption spectra of these optical glasses were measured on a Perkin-Elmer Lambda 25 UV-VIS-NIR Spectrophotometer, and show a sharp absorption edge at around 350 nm wavelength. The structural characterization of the as-cast glass samples was carried out using XRD technique. The XRD investigations were obtained in a Philips Model PW3710 using CuK_α radiation at 40 kV and 40 MV settings in the 2θ range from 10° to 90°. The crystallization phases were identified by comparing the peak positions, and intensities with those in the JCPDS (Joint Committee on Powder Diffraction Standards) data files. The Fourier transform (FT) infrared spectra were recorded with Perkin Elmer FT-IR spectrometer in the 1200–300 cm^{-1} range, by using KBr pellets technique. The structure of these tellurite glass samples was measured by FT-Raman spectrophotometer (RENISHAW in via Raman Microscope) within the range of 0–1200 cm^{-1}. The Vickers hardness, H_v, at room temperature was measured using INSTRON, Wilson-Wolpert Tukon 2100B in air. The applied loads were in the range of 5–10 N, and the time of loading was 10 s. A diamond Vickers indenter tip was used with a geometrical correction procedure for accurate calculation of hardness. During the measurements of the Vickers hardness, the geometrical correction procedure was employed for each well-polished samples which have a size 1.0×6.0 cm^2 and the measurements repeated for three different samples.

3. Results

3.1. Thermal properties

Fig. 1(a1) and (a2) shows the DSC curves of $1.0Bi_2O_3$-19ZnO-$80TeO_2$ glasses at 800, 875, 1000, 1025, and 1050 °C, and $0.2Bi_2O_3$-19.8ZnO-$80TeO_2$ glass at 1025 °C melting temperatures for the prepared glass samples. From DSC scans, the glass transition, T_g, onset crystallization, T_x, peak and melting temperatures, T_m, were determined as seen in Table 2.

As could be seen from Table 2, and Fig. 1, the T_g, T_x values are increasing gradually with an increase in the casting temperatures except for 1025 °C.