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Physical properties of B_2O_3–TeO_2–Bi_2O_3 glass system

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ABSTRACT

Boro-tellurite glass system with different concentrations of Bi_2O_3 had been prepared and characterized. The FTIR analysis indicated a glass former role of Bi_2O_3 that was deduced from the formation of [BiO_3] structural units. These units transformed the structural units [TeO_3] into [TeO_4] and [BO_3] into [BO_4]. This process increased the environment of bridging oxygens that increased the density and decreased the molar volume of the glass structure. The increase of the ultrasonic velocities, the elastic moduli (experimentally determined and theoretically computed according to Makishima-Mackenzie model) with the addition of Bi_2O_3 was attributed to the increased compactness and rigidity. The increment coordination number increased the cross-link density and improved the glass transition temperature. The hyper-polarizability of Bi^{3+} due to the d-orbital contribution increased the crystallization peak and enhanced the thermal stability.

1. Introduction-

Nowadays, the physical, optical, mechanical and magnetic properties of borate and boro-tellurite glasses are widely investigated because of their scientific advantages and potentials in the fiber optic communication systems, nonlinear optical devices and lasers [1–3]. The network of glasses comprised two glass formers such as TeO_2 and B_2O_3 had distinct optical, electrical, thermal and mechanical properties. The networks of boro-tellurite based glasses are characterized with the low melting temperature, the high transparency and stable against devitrification. Thus, the study of the structure of a binary B_2O_3–TeO_2 glass system showed that the network was composed of TeO_4, BO_3 and B_3O_6 structural units that affected the distances between B–O, O–O, Te–Te and Te–O bonds and the glass densities of this system show increment with the increasing amount of TeO_2 [4]. Elkhoshkhany et al. [5], found that the optical energy gap and the band tailing of lithium boro-tellurite glass system decreased while the glass transition (T_g) and crystallization (T_c) temperatures increased and attributed this process to the creation of non-bridging oxygens and the increment of the degree of disorder of the network as a function of B_2O_3. The FTIR of zinc boro-tellurite glasses [6] doped with Ho^{3+} ions indicated the transformation of TeO_3 into TeO_4 and BO_3 into BO_4 structural units with the increase of Ho_2O_3. This process increased the content of the bridging oxygens that increased the oxygen packing density, the density and the refractive index and decreased both of the molar volume and the indirect optical band gap energy.

The presence of B_2O_3 and TeO_2 in boro-tellurite glasses caused a complex specification in the glass structure, so that, a heavy metal oxide (HMO) such as Bi_2O_3 can be added to the glasses to increase its density and improve its structural and optical properties. Bi_2O_3 is considered as a harmless, non-carcinogenic material, and is valuable in electronic applications, ceramic production, shielding for radiation, non-linear optical devices and good element for “warm” superconductors because of the high polarizability that originated from its empty d-orbits [7–11]. The addition of Bi_2O_3 in boro-tellurite glasses produced a faint-yellow color as reported by Hasegawa [12]. The yellowish color was attributed to the Bi-reduction in the case of high melting temperature (> 900 °C) or corrosion of the crucible. Moreover, the optical absorption edge was shifted to longer wavelength with the increasing of Bi_2O_3 content. The shift of the absorption edge corresponded to the increase of the concentration of non-bridging oxygen (NBO). On the other hand, Munoz-Martín et al. [13] reported on tellurite glasses containing HMO. They [13] found that the increase of HMO either WO_3 or PbO increased the glass network connectivity, the formation of [TeO_3] (tp) units, the glass transition temperature and more decrease of TeO_2 will deform the network. This confirmed that

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Table 1
The nominal chemical composition of the prepared glasses (mol%).

Glass No.	Chemical composition		
	B_2O_3	TeO_2	Bi_2O_3
G1	10	50	40
G2	10	40	50
G3	10	30	60
G4	10	20	70
G5	10	10	80

W^{6+}-ions are incorporated as network formers, alternating with Te^{4+}-ions, forming mixed Te–O–W and W–O–W linkages. Thus, the glasses included HMO such as Bi_2O_3, WO_3 or BaO are considered as lead-free glass systems. These glasses offer comparable gamma radiation shielding materials and better electron stopping properties of lead free glass systems than lead based glasses [14, 15]. Accordingly, in this study, bismuth boro-tellurite glasses containing different concentrations of Bi_2O_3 were checked and analyzed. The analysis will be performed using FTIR, ultrasonic and DTA techniques.

2. Experimental procedures

The boro-tellurite glasses modified with Bi_2O_3 had the chemical formula $(90 - x)$ TeO_2–$10B_2O_3$–xBi_2O_3 ($40 \le x \le 80$ mol%) had been prepared using reagent grade H_3BO_4, Bi_2O_3 and TeO_2 by the melt quenching technique. The used chemicals with purity 99.95% were purchased from Sigma. The nominal compositions were listed in Table 1. The specified quantities of the mentioned chemicals were mixed completely and then contained in a ceramic crucible. The powder samples were melted in an electrically heated furnace at about 900 °C for 1 h and the melt was then cast onto preheated stainless-steel mold, which was transferred immediately to the annealing furnace adjusted at 275 °C for one hour. The obtained glasses were lapped, and two opposite sides were polished to be suitable for the use in the ultrasonic velocity measurements.

X-ray diffraction patterns were obtained by using Philips X-ray diffractometer (PW/1710 with Ni-filtered Cu-K_α and radiation $\lambda = 1.542$ Å). The thermal properties of these glasses as a function of Bi_2O_3 were determined by the differential thermal analyzer system (SHIMADZU 50 DTA). The 10 mg powdered glass sample was placed in a platinum crucible and examined in Argon medium with a heating rate 10 K/min. The powdered alumina was used as a reference material. The accuracy in the measurements of T_g is ± 2 K.

The Fourier Transform Infrared (FTIR) spectra of the samples were scanned in the range 400–1600 cm^{-1} on JASCO 430 (Japan) spectrometer at room temperature. The accuracy of the measurement was about 2 cm^{-1}. The density (ρ) of the glass samples was determined by using the Archimedes technique. Toluene was used as the buoyant liquid. Considering the molar weight of the glass samples (M), the molar volume, V_m, can be determined as M/ρ. The accuracy in the measurements of the density and the determination of the molar volume were about ± 0.21 g/cm^3 for the density and ± 0.35 × 10^{-6} m^3/mol for the molar volume.

The ultrasonic measurements were performed at room temperature by a system consisted of the Echo - graph (Krautkramer model USM3 pulsar /receiver instrument) and two transducers. The operated frequency was adjusted to 4 MHz. The was used for the determination of the longitudinal (v_L) and shear (v_T) velocities. Random errors in the measurements of the velocities were ± 10 m/s. The two velocities besides the density were utilized in determining the longitudinal elastic moduli (L), shear elastic moduli (G), bulk modulus (K), Poisson's ratio (σ) and Young's modulus (Y) as;

Longitudinal elastic moduli L = ρv_L^2Shear elastic moduli G = ρv_T^2.

Bulk modulus K = L-4/3GPoisson's ratio (σ)$\sigma = \frac{L-2G}{2(L-G)}$and Young's modulus Y = (1 + σ) 2G.

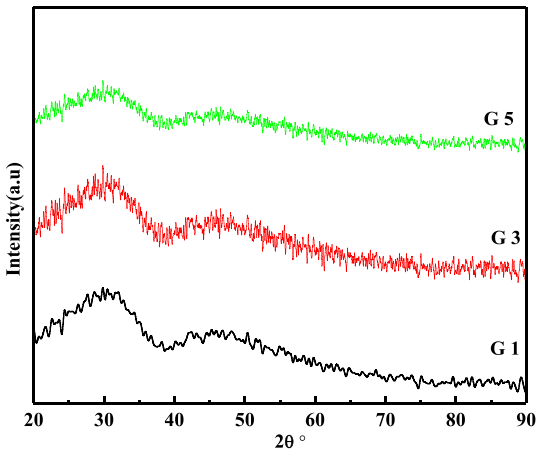

Fig. 1. XRD of the $(90 - x)$ TeO_2–$10B_2O_3$–xBi_2O_3 (x = 40, 60 and 80 mol%) glass system.

3. Results and discussions

Neither discrete lines nor sharp peaks were revealed in the XRD curves as shown in Fig.1. Only a hump about 30° demonstrated the amorphous state of the prepared glass samples was observed [3, 5, 8].

3.1. FTIR analysis

The FTIR analysis is a useful tool for studying the structure and the dynamics of the glasses. The FTIR spectra of the present glass system were plotted in Fig. 2. The plotted broad bands of the spectra were deconvoluted into several symmetrical Gaussian bands to find out the molecular vibrations and the structural units by a deconvolution process technique [16] that considering the position and the area of each band related to the vibrations of a particular structural unit. The deconvolution process was performed by using the Origin software version 8.5. The Origin fit function determined the correlation coefficient

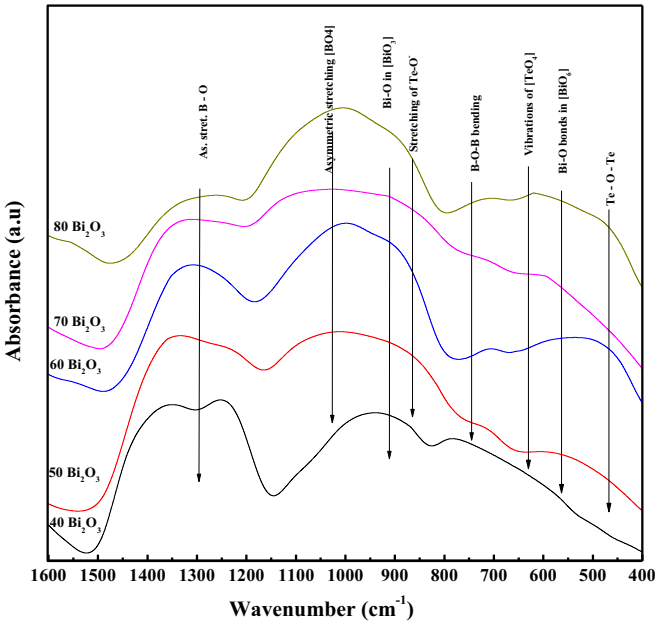

Fig. 2. Infrared spectra of the $(90 - x)$ TeO_2–$10B_2O_3$–xBi_2O_3 ($40 \le x \le 80$ mol %) glass system.