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Elastic moduli of borosilicate glasses doped with heavy metal oxides

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ABSTRACT

Comparative studies on the theoretical and experimental values of elastic moduli of the borosilicate glasses (70-*x*) SiO_2–$30B_2O_3$–*x*HMOs glass system, where HMOs (heavy metal oxides) are TiO_2, BaO and Bi_2O_3 with 0, 1, 2, 3, 4 and 5 mol% of each HMO, were investigated. Elastic moduli were assessed by measuring the ultrasonic velocities. The number of network bonds per unit volume, the average of a stretching force constant, the average of cross-link density, the average of ring diameter and the theoretical bond compression bulk modulus were calculated by using a theoretical bond compression model to confirm the obtained results from the experiments. The results show that changes in the structure of the glass depend on a type and concentration of HMOs. Moreover, the experimental elastic moduli are in good agreement with the theoretical values.

1. Introduction

Glass is a solid material of interest because it is transparent to visible light and is a good insulator. Of specific interest for a glass material, borosilicate glasses have high chemical and mechanical resistance, very low electrical conductivity and thermal expansion coefficient. Thus, they are widely used in laboratory, optical, heat-resistant, fiber, pharmaceutical and sealing glass applications, and even for nuclear waste immobilization [1–4].

Elastic properties are very informative regarding the structures of glasses and they are directly related to the interatomic potentials. The glasses are isotropic and have only two independent elastic constants: longitudinal and shear moduli. These parameters are obtained from calculating the longitudinal and shear velocities and the densities of the glasses. The bulk modulus, Young's modulus and Poisson's ratio can also be deduced. The elastic moduli of borosilicate glasses containing transition, rare earth and/or heavy metal oxide (HMO) depend on ultrasonic waves at room temperature and were previously reported by several groups [4–15].

The glasses based on heavy metal oxides (HMOs) such as BaO, Bi_2O_3, PbO, TiO_2, Ag_2O, etc. have always been an area of interest because of their characteristic structural and physical properties such as high refractive index, high thermal expansion, high density, low transformation temperature and excellent infrared transmission (IR). Therefore, these glasses have been desirable aspirants for potential applications in IR technologies, design of laser devices and non-linear optics [16,17]. Among HMO glasses, bismuth and/or barium borosilicate glasses are the subject of growing and intense research. The glasses containing BaO and/or Bi_2O_3 have attracted considerable attention because of their vast range of applications in the fields of radiation shielding, glass-ceramics, reflecting windows, thermal and mechanical sensors, etc. [18–20]. In addition, the glasses containing significant concentrations of transition metal oxides (TMOs) such as TiO_2, ZnO, Fe_2O_3, V_2O_5, MnO_2, etc. are of continuing interest because of their applicability in memory switching, electrical threshold, optical switching devices, etc. [21–25].

In this work, the elastic moduli of borosilicate glasses will be discussed. Information regarding the number of network bonds per unit volume, the average of stretching force constant, the average of ring size diameter and the average of the cross-link density will be examined and discussed. The theoretical values of bond compression bulk modulus and elastic moduli will be calculated and compared with the experimental values.

2. Materials and methods

2.1. Preparation of glass samples

Rectangular shaped glass samples of the (70-*x*)SiO_2–$30B_2O_3$–*x*HMOs glass system (where HMOs are TiO_2, BaO and Bi_2O_3 with 0, 1, 2, 3, 4 and 5 mol% of each HMO) were prepared by the conventional melting technique. The oxides of SiO_2, B_2O_3, TiO_2, BaO and Bi_2O_3 used in this work were of an analytical regent grade. To prepare the glass samples, appropriate amounts of SiO_2, B_2O_3, TiO_2, BaO and Bi_2O_3 were weighed using an electronic balance with the accuracy of the order of 0.0001 g. The homogeneous mixtures were placed in ceramic crucible and melted in an electric furnace until homogeneity of the glass melt was ensured. The melted glasses were poured into graphite molds and annealed for 2 h before naturally cooling down to room temperature.

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2.2. Density and molar volume measurements

The densities of the glass samples were determined by Archimedes' principle, using n-hexane as an immersion liquid and applying the relationship (1) [6]

$$\rho = \rho_L\left(\frac{W_a}{W_a - W_b}\right) \tag{1}$$

where ρ_L is density of the immersion liquid, and where W_a and W_b are the sample weights in air and in the immersion fluid, respectively. The experiment was repeated three times to obtain an accurate value for the density. The estimated error in these measurements was about ± 0.015 g cm^{-3} (shown in Table 1). The molar volume (V_a) was calculated from the expression $V_a = \frac{M}{\rho}$, where M is the molecular weight of the glass, which was calculated according to the relationship $M = \sum x_i M_i$ [26], where x_i is the mole fraction of the component oxide i and M_i is its molecular weight. The glass packing density can be calculated from the following Eqs. (2)–(3) [7]

$$V_t = \frac{\rho}{M}\sum_i x_i V_i \tag{2}$$

where V_i is given by,

$$V_i = \frac{4\pi N_A}{3}\left(x r_M^3 + y r_O^3\right) \tag{3}$$

where N_A is Avogadro's number, and where r_M and r_O are the ionic radii of the cation and anion of the oxide M_xO_y, respectively. The uncertainties in molar volume and packing density were acquired from experiments repeated three times of densities. The estimated error in these results was about ± 0.200 cm^3·mol^{-1} and $\pm 0.003 \times 10^{-6}$ m^3, respectively (shown in Table 1).

2.3. Ultrasonic measurements and determination of elastic moduli

To measure the ultrasonic velocity in the glass samples, an ultrasonic flaw detector, SONATEST Sitescan 230, was used. The ultrasonic wave was generated from a ceramic transducer with a resonant frequency at 4 MHz and acting as a transmitter–receiver at the same time. The ultrasonic wave velocity (v) can be calculated using the following Eq. (4) [5]:

$$v = \frac{2x}{\Delta t} \quad \left(cm{\cdot}s^{-1}\right) \tag{4}$$

where x is the sample thickness (cm) and Δt is the time interval (s). The measurements were repeated three times to check the reproducibility of the data. The estimated error in the velocity measurements was ± 23 m·s^{-1} for the longitudinal velocity and ± 11 m·s^{-1} for the shear velocity. The elastic strain produced by a small stress can be described by two independent elastic constants, C_{11} and C_{44} [27]. Elastic moduli were calculated using the following standard relations (5)–(10) [27]:

$$\text{Longitudinal modulus } C_{11} = L = \rho v_L^2, \tag{5}$$

$$\text{Shear modulus } C_{44} = G = \rho v_S^2, \tag{6}$$

$$\text{Bulk modulus } K = L - \frac{4}{3}G, \tag{7}$$

$$\text{Young's modulus } E = (1+\sigma)2G, \tag{8}$$

$$\text{Poisson's ratio } \sigma = \frac{L-2G}{2(L-G)}, \tag{9}$$

$$\text{Microhardness } H = \frac{(1-2\sigma)E}{6(1+\sigma)}, \tag{10}$$

Debye temperature calculated from Eq. (11) [28]

$$\theta_D = \left(\frac{h}{k_B}\right)\left(\frac{3zN_A}{4\pi V_a}\right)^{1/3} v_m, \tag{11}$$

where v_L and v_S are longitudinal and transverse velocities, respectively. h is Planck's constant, k_B is Boltzmann's constant, N_A is Avogadro's number, z is the number of atoms in the chemical formula and v_m is the mean ultrasonic velocity defined by the relationship (12) [29].

$$v_m = \left[\frac{3v_L^3 v_S^3}{v_L^3 + v_S^3}\right]^{1/3} \tag{12}$$

Softening temperature T_s is related to the ultrasonic velocity of shear waves v_S by Eq. (13) [4]

$$T_s = \frac{v_S M}{C^2 Z} \tag{13}$$

where Z is the number of atoms in the chemical formula and C is the constant of proportionality and equals 507.4 $m{\cdot}s^{-1}{\cdot}K^{1/2}$. The

Table 1
Glass composition, density (ρ), molar volume (V_a) and packing density (V_t) of the glass samples.

Sample no.	SiO_2 (mol%)	B_2O_3 (mol%)	TiO_2 (mol%)	BaO (mol%)	Bi_2O_3 (mol%)	ρ (g·cm^{-3})	V_a (cm^3·mol^{-1})	$V_t \times 10^{-6}$ (m^3)
S0	70	30	0	0	0	2.548	24.704	0.485
S1–TiO_2	70	30	1	0	0	2.547	24.287	0.498
S2–TiO_2	70	30	2	0	0	2.572	23.821	0.512
S3–TiO_2	70	30	3	0	0	2.594	23.390	0.526
S4–TiO_2	70	30	4	0	0	2.614	22.985	0.540
S5–TiO_2	70	30	5	0	0	2.634	22.585	0.555
S1–BaO	70	30	0	1	0	2.582	24.933	0.485
S2–BaO	70	30	0	2	0	2.600	25.023	0.488
S3–BaO	70	30	0	3	0	2.630	25.189	0.489
S4–BaO	70	30	0	4	0	2.647	25.381	0.489
S5–BaO	70	30	0	5	0	2.671	25.503	0.491
S1–Bi_2O_3	70	30	0	0	1	2.676	24.132	0.501
S2–Bi_2O_3	70	30	0	0	2	2.800	23.645	0.516
S3–Bi_2O_3	70	30	0	0	3	2.947	23.020	0.535
S4–Bi_2O_3	70	30	0	0	4	3.021	22.996	0.540
S5–Bi_2O_3	70	30	0	0	5	3.123	22.767	0.551
The uncertainty						±0.015	±0.200	±0.003