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ELASTIC CONSTANTS OF Tm-DOPED GLASS BY BULK COMPRESSION MODEL

Hasnimulyati Laoding[1], Halimah Mohamed Kamari[1], Azmi Zakaria[1], Abdul Halim Shaari[1] and Ishak Mansor[2]

[1]*Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.*

[2]*Technical Support Division, Malaysian Institute for Nuclear Technology Research (MINT), Bangi, Kajang, Malaysia.*

Corresponding author:halimahmk@upm.edu.my

ABSTRACT

Tm_2O_3-ZnO-B_2O_3-TeO_2 glass system was prepared by using melt quenching technique. The basic measurements of the glass that are density and molar volume were measured. Elastic properties of Tm-doped zinc borotellurite glass were investigated using bulk compression model. After considering all the factors that involve in this theoretical approach such as cross-link density, number of bond per unit volume and stretching force constant, all the elastic moduli can be calculated. This includes bulk, shear, Young Modulus and also Poisson's ratio. Besides that, the atomic ring size also can be determined. Results indicated that the bulk modulus, K_{bc} decreased while the other elastic moduli increased with the increment of Tm^{3+}. The Poisson's ratio is decreased as Tm^{3+} is added. Results show that the network structure of the glass samples become more compact and rigid as Tm^{3+} is added.

Keywords: Tm-doped; bulk compression; elastic; density; molar volume; average cross-link density;

INTRODUCTION

Elastic constants are the values that used to describe stress-strain relationship in a material. There are four types of elastic constants that widely known that are longitudinal modulus, shear modulus, bulk modulus and also Young's modulus. Generally, high elastic moduli explain that a material can withstand a high force and produce just a little strain when force is applied. On the other hand, low elastic moduli means that a material will produce a big strain when force is applied to it. Rubber for example, has a low elastic moduli and that is the reason why rubber can stretch when pulled and then return back to its original form when the force is removed.

Bulk compression model (also known as bond compression model) is a model that proposed by Bridge in 1983 [1] that explain about properties of glass by considering the atomic structure of each component in the sample. The factors include the number of bonds per unit volume (n_b), the number of bridging bonds per cation and the stretching force constant (F). In this model, they assume that an isotropic deformation will only change the network bond length and not the bond angle. Using all the factors listed above, they formulated an equation to find the bulk modulus (K_{bc}) and the other moduli are calculated from the K_{bc} value.

Some research had been done on elastic properties of rare earth doped glasses. In earlier works, Mallawany et al. [2] studied the elastic constants of La_2O_3, CeO_2, Sm_2O_3, Er_2O_3, and Y_2O_3- doped glass. However, the information on elasticity of Tm-doped glass is still not available. This is the reason why this study is being done. The objective of this work is to investigate the elastic properties of Tm-doped glass by using bulk compression model.

METHODOLOGY

Glasses of TeO_2-B_2O_3-ZnO-Tm_2O_3 series had been prepared using melt-quenching technique. High purity chemicals were used that are TeO_2 (99.99%, Alfa Aesar Company), B_2O_3 (97.5%, Alfa Aesar Company), ZnO (99.99%, Alfa Aesar Company), and Tm_2O_3 (99.9% Alfa Aesar Company). The chemicals were weighted and ground in mortar to produce a homogenous mixture. It was then placed in alumina crucible and pre-heated in furnace at 400°C for one hour. This was done in order to eliminate any water vapour inside the crucible. After that, the mixture was melt in the second furnace at 900°C for one hour. Next, the molten was poured into mould that had been pre-heated at 400°C to undergo annealing process. After two hours, the furnace was turned off and the sample was cooled down for 24 hours.

Density and molar volume of the glass was measured using densitometer with a simple Archimedes principle using distilled water as the immersion liquid. The equation to calculate the density according to Azianty et al in 2013 [3] is as stated below:

$$\rho = \frac{m_a}{m_a - m_w}\rho_w \tag{1}$$

where m_a, m_w and ρ_w is mass in air, mass in water and density of water respectively. The molar volume, V_m of the glass was calculated using the following relation:

$$V_m = \frac{M_T}{\rho} \tag{2}$$

$$M_T = \sum x_i M_i \tag{3}$$

where M_T is the total molecular weight of the glass sample, x_i is the molar fraction of each component and M_i is the molecular weight of each oxide.

In bulk compression model, the values that need to be calculated are average cross-link density ($<n_c>$), total number of cations per unit glass formula unit (η), average stretching force constant (F) and number of network bond per unit volume (n_b). The equations that were used in the calculation are as follows:

$$< n_c > = \frac{1}{\eta} \sum_i x_i (n_c)_i (N_c)_i \tag{4}$$

where η is the total number of cations per unit glass formula unit, n_c is the number of cross-links per unit cation which is equal to number of bonds minus by 2 and N_c is the number of cations per unit glass formula unit. The formula to calculate η is:

$$\eta = \sum_i x_i (N_c)_i \tag{5}$$

Average stretching force constant can be calculated using the relation below:

$$F = \frac{\sum_i xnf}{\sum_i xn} \tag{6}$$

$$f = \frac{1700}{r^3} \text{ (N m}^{-1}\text{)} \tag{7}$$

where n, f and r is the coordination number, first order stretching force constant and bond length (in Å) respectively. The number of network bond per unit volume, n_b can be calculated using the relation:

$$n_b = \frac{N_A}{V_m} \sum x_i (n) \tag{8}$$

where N_A is the Avogadro constant. The bulk modulus and the Poisson's ratio then can be calculated using the following formula:

$$K_{bc} = \frac{\rho N_A}{9M} \sum_i x_i (n) r^2{}_i f_i \tag{9}$$

$$\sigma_{bc} = 0.28(< n_c >)^{-0.25} \tag{10}$$

The other elastic moduli can be calculated based on the value of K_{bc} and σ_{bc}:

$$G_{bc} = 1.5 K_{bc} \left[\frac{1-2\sigma_{bc}}{1+\sigma_{bc}}\right] \tag{11}$$

$$L_{bc} = K_{bc} + 1.33 G_{bc} \tag{12}$$

$$E_{bc} = 2 G_{bc} (1 + \sigma_{bc}) \tag{13}$$

The atomic ring size also can be determined in this model using the relation below:

$$l = \left(0.0106 \frac{F}{K_g}\right)^{0.26} \tag{14}$$

RESULT AND DISCUSSION

The density of $\{[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.7}[ZnO]_{0.3}\}_{1-x}\{Tm_2O_3\}_x$ glass increases linearly from 4.62 to 4.99 g/cm^3 as Tm_2O_3 replaced TeO_2-B_2O_3-ZnO in the glass system. Molar volume was calculated using Eq.(2) with consideration of the measured density. It is found that it varies between 25.94 and 26.21 cm^3/mol and increasing with addition of Tm_2O_3 as shown in Fig 1. Table 1 gives the value of density (ρ) and molar volume (V_m) of all glass samples.

Table 1: Density, ρ and molar volume, V_m of glass samples

Tm_2O_3 composition (mol)	ρ (g/cm^3)	V_m (cm^3/mol)
0.01	4.62	25.94
0.02	4.71	26.01
0.03	4.80	26.11
0.04	4.90	26.13
0.05	4.99	26.21

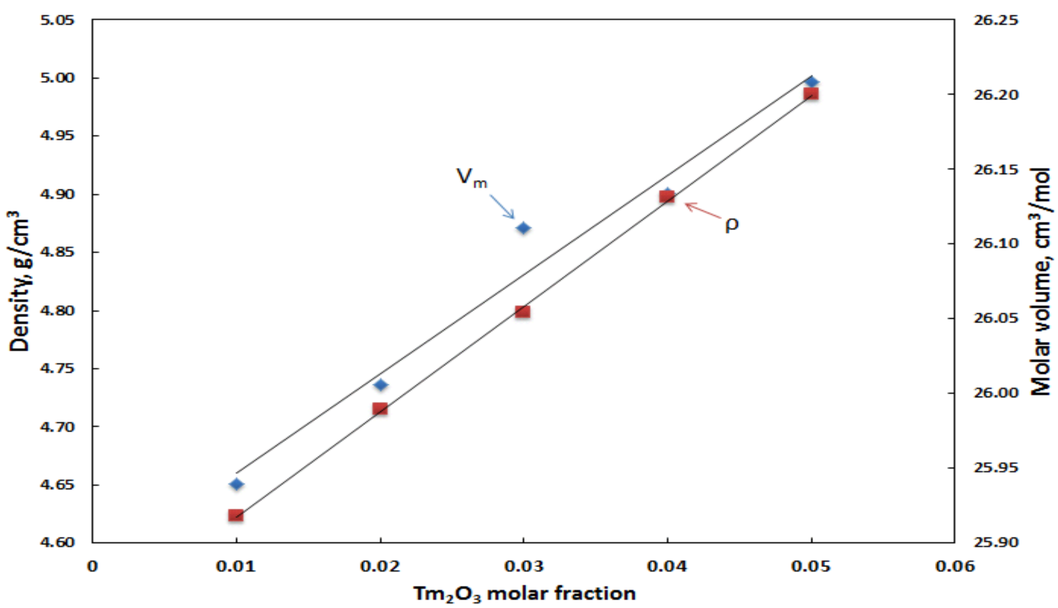

Figure 1: Variation of density and molar volume of $\{[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.7}[ZnO]_{0.3}\}_{1-x}\{Tm_2O_3\}_x$ glass system

The increment of density is due to higher molecular weight of thulium oxide compared to the other component used in the glass system. As the lighter atom is replaced with the heavier atom, it causes the glass produced to be denser as the total molecular weight of the glass is increased. This is also in accordance to the formula of density that density is directly proportional to mass. Besides that, the additional ion might fill the interstitial spaces of the network and causes the density to be increased. The same trend is also reported by the previous researchers that added rare earth oxide in their glass system such as Baizura et al. [4] and Rada et al. [5] in 2011.

The rise of molar volume indicates that there exists an increment of free volume in the glass network. The radial bond length or interatomic spacing of thulium as stated in Table 2 is large. Thus, the addition of Tm_2O_3 will cause the free volume inside the glass system to be increased and at the same time increase the molar volume of the glass sample [6]. The higher coordination number of thulium also might be a contributing factor to this situation. [7]

Total number of cations per unit glass formula unit (η), average cross link density ($<n_c>$), average stretching force constant (F) and number of network bond per unit volume (n_b) are listed in Table 3. Average cross-link density showed an increase from 2.179 to 2.297 with the addition of Tm_2O_3 into the glass system as shown in Figure 2. The enhancement of $<n_c>$ may be due to the increment of dimensionality as Tm_2O_3 with 6 coordination number replacing the other compounds that have less coordination number. The change in coordination number of tellurium and borate in the glass system also can be a factor to the augmentation in dimensionality of the glass system [8]. The increment of average cross-link density also may be due to the decrement of non-bridging oxygen in the network as reported by Samir in 2009 [9]. According to Yousef et al. (2006) [10], average cross-density can also be related to the change in average ring size of the network. This will be discussed later in this paper.

Figure 3 shows that n_b has an increasing trend while F has an opposite trend as Tm_2O_3 replaced the other compound in the glass. This value is calculated using information that listed in Table 2 that gives the coordination number (n) for each oxide. The increment of n_b shows that as Tm_2O_3 is added, it causes the glass network to link to one another and as a result producing a rigid glass. The same result is reported by Cilekbilek et al. in 2013 as WO_3 and Li_2O is added to tellurite glass system [11].

Table 2: Coordination number (n), number of cross-links per unit cation (n_c), number of cations per unit glass formula unit (N_c), bond length (r) and first order stretching force constant (f) of each oxide

Oxide	n	n_c	N_c	r (Å)	f (Nm^{-1})
TeO_2	4 [12]	2	1	1.98 [1]	219.00
B_2O_3	3 [12]	1	2	1.37 [13]	668.42
ZnO	6 [12]	4	1	1.99 [1]	216.37
Tm_2O_3	6 [14]	4	2	2.14 [15]	173.46

The decrement of average stretching force constant, F as shown in Figure 3 attributed to the change in the type of bonds in the glass network, from covalence to ionic. As Tm_2O_3 with weak Tm-O bonds replace TeO_2, B_2O_3 and ZnO that have stronger bonds, it would lead to the rise of ionic cross-links and rigidity and at the same time decrement of F. Value of F also are governed by the reciprocal of the bond length. As stated in Table 2, Tm_2O_3 has the longest bond length compared to the other compounds. As a result, the first order stretching force constant (f) of thulium is the lowest among the other compounds. Thus, as thulium is added to the glass network, it will cause the average stretching force constant to be decreased [13].

Table 3: Total number of cations per unit glass formula unit (η), average cross link density ($\langle n_c \rangle$), average stretching force constant (F) and number of network bond per unit volume (n_b) for all glass samples

Tm_2O_3 composition (mol)	η	$\langle n_c \rangle$	F (Nm^{-1})	n_b ($x10^{23}$ cm^{-3})
0.01	1.2179	2.1792	280.9363	1.0231
0.02	1.2258	2.2092	279.4633	1.0242
0.03	1.2337	2.2388	278.0011	1.0238
0.04	1.2416	2.2680	276.5495	1.0266
0.05	1.2495	2.2969	275.6774	1.0274

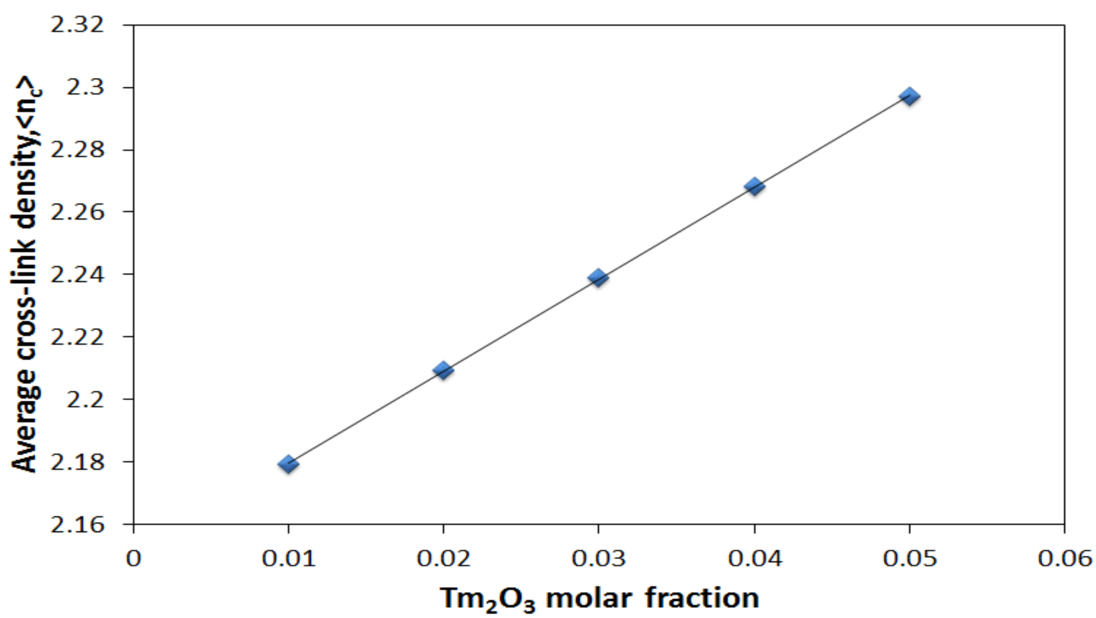

Figure 2: Average cross-link density of glass samples

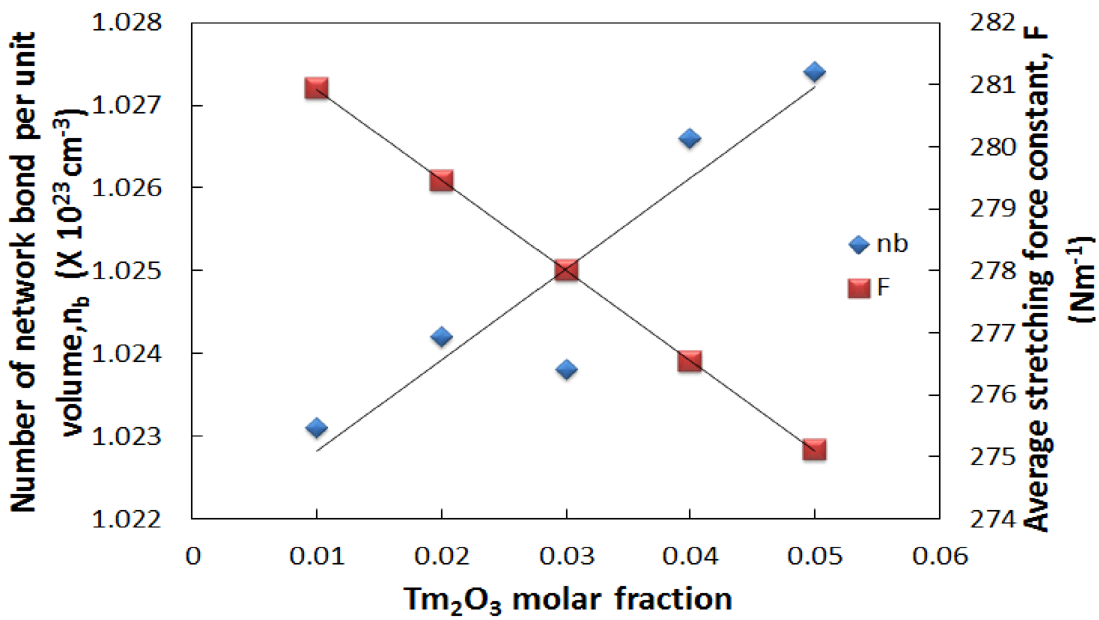

Figure 3: Variation of number of network bond per unit volume, n_b and average stretching force constant, F

Table 4: Bulk modulus (K_{bc}), Shear modulus (G_{bc}), Longitudinal modulus (L_{bc}), Young's modulus (E_{bc}), Poisson's ratio (σ_{bc}), ratio K_{bc}/K_e and atomic ring size (l) of Tm-doped glass

Tm_2O_3 composition (mol)	K_{bc} (GPa)	G_{bc} (GPa)	L_{bc} (GPa)	E_{bc} (GPa)	σ_{bc}	K_{bc}/K_e	l (nm)
0.01	103.56	68.06	194.08	167.49	0.230	2.498	0.504
0.02	103.48	68.25	194.25	167.84	0.229	2.395	0.498
0.03	103.28	68.35	194.18	167.99	0.229	2.347	0.495
0.04	103.39	68.65	194.71	168.64	0.228	2.316	0.493
0.05	103.27	68.80	194.77	168.89	0.227	2.316	0.492

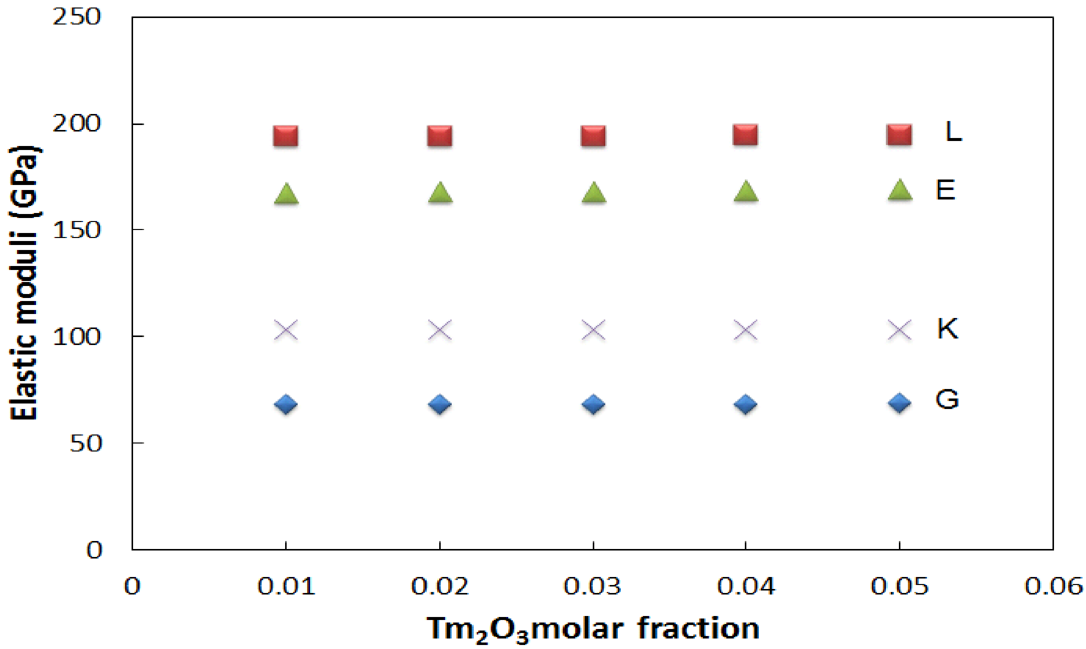

Figure 4: Value of elastic moduli vs Tm_2O_3 molar fraction

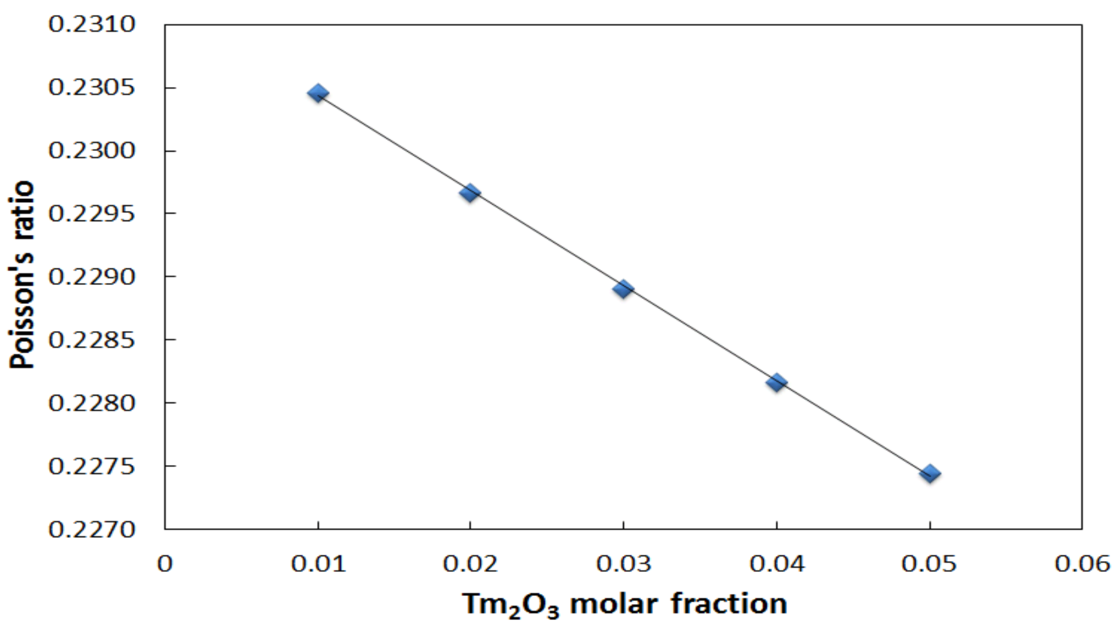

Figure 5: Poisson's ratio vs Tm_2O_3 molar fraction

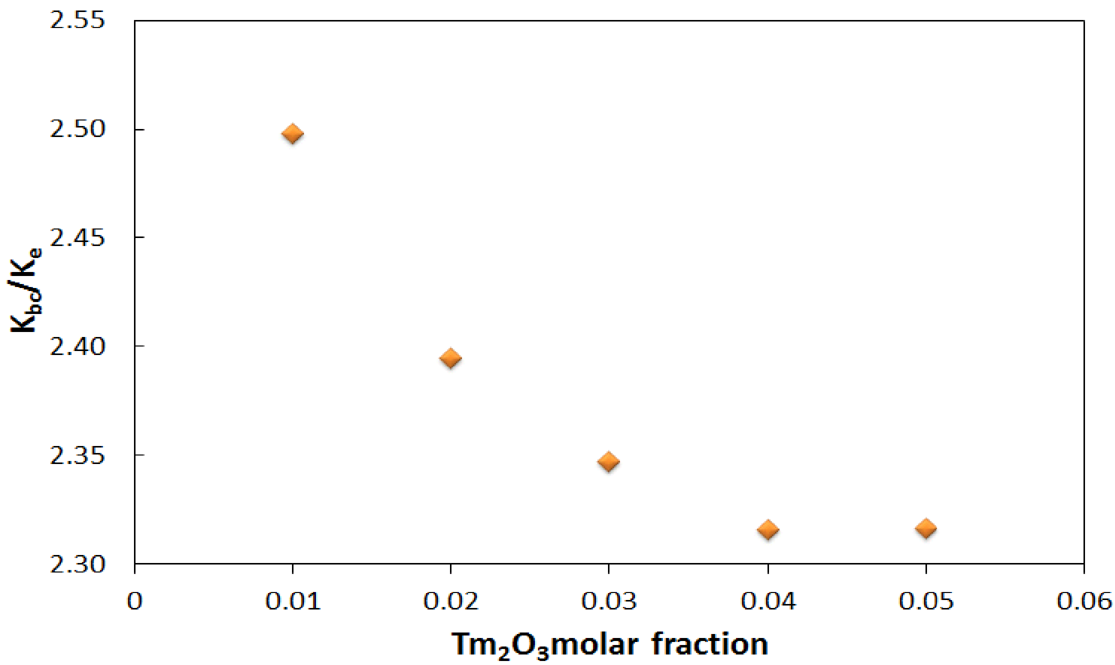

Figure 6: Ratio K_{bc}/K_e of $\{[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.7}[ZnO]_{0.3}\}_{1-x}\{Tm_2O_3\}_x$ glass

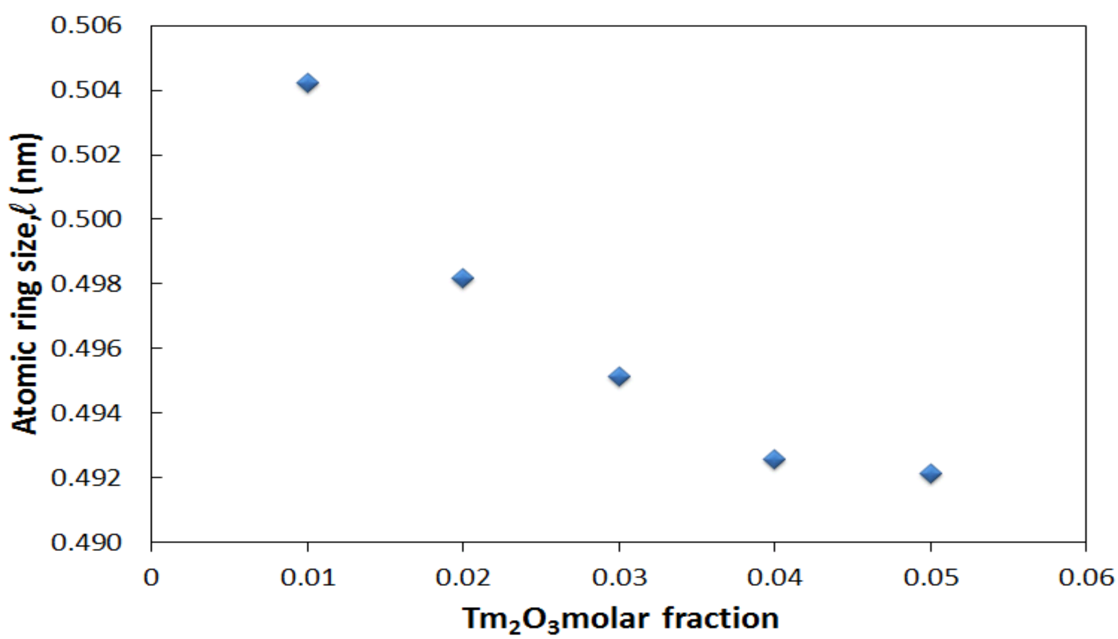

Figure 7: Atomic ring size, l of Tm-doped glass

According to this model, the value of bulk modulus, K_{bc} is mainly depends on n_b and f [7, 16]. In this study, K_{bc} value is dependent on the value of F. As shown in Table 4, the value of K_{bc} is decreasing with the increment of thulium oxide in the sample. This may be due to the decrement in average stretching force constant, F of the glass sample. As F is decreased, it causes K_{bc} to be decreased and as a result make the glass less rigid. However, the other calculated elastic moduli show an opposite trend to K_{bc}. Shear modulus (G_{bc}), Young modulus (E_{bc}) and longitudinal modulus (L_{bc}) show an increasing trend as Tm_2O_3 is added. This may be attributed to the increment in the number of network bond per unit volume. As all the value of elastic moduli is compared, L_{bc} shows the highest value while G_{bc} shows the smallest value. Thus, it can be concluded that the glass system is able to withstand longitudinal stress better than shear stress. The value of K_{bc} also is lower compared to E_{bc}. This indicates that the glass samples can tolerate stress in one direction better than stress that acting in all directions [16].

Literally, Poisson's ratio is the ratio of lateral to longitudinal strain. This value is very dependent on the average cross-link density because the lateral strain will be reduced as $\langle n_c \rangle$ is increased. As $\langle n_c \rangle$ in this study is increased, it indicates that the glass network has more linked. The lateral strain then will be decreased and so does the Poisson's ratio [1]. The reduction of Poisson's ratio as shown in Figure 5 confirms the increment in rigidity and cross-link density of these glasses as the type of bond is changing from covalence to ionic [13].

Ratio of K_{bc}/K_e is a measure of the extent to which bond bending is governed by the configuration of the network bonds. K_{bc}/K_e is expected to increase with atomic ring size of a network. When ratio K_{bc}/K_e is equal or more than 1, it indicates that the network is an open and large-ringed. If the value reaches 3 to 10, it indicates that network bond bending (or non-network bond compression) processes predominate when these materials are subjected to bulk compression [1]. Figure 6 shows that K_{bc}/K_e for Tm-doped glass is decreasing with the increment of Tm_2O_3. The value is reduced from 2.498 to 2.316. This specifies that ideal isotropic compression mechanism dominating the glass network [17]. Besides that, the reduction also confirms the increment in rigidity of the glass samples.

Atomic ring size of the network is calculated using Equation (14) and assumed to have direct relationship with ratio K_{bc}/K_e [18]. Besides that, it is also related to the average cross-link density of the glass [10]. The decrement of atomic ring size as shown in Figure 7 proves the increment in rigidity of the glass and the value is directly proportional to ratio K_{bc}/K_e. It is also indicates that the structure become more closed with the addition of Tm_2O_3 and consequently the increment in cross-link density [9].

CONCLUSION

In this study, elastic properties of TeO_2-B_2O_3-ZnO-Tm_2O_3 glasses were investigated and analyse using bulk compression model. Based on the data, it is found that as Tm_2O_3 is added to the glass composition, average cross-link density of the glass network is increasing. Average stretching force constant of the glass series has a decreasing trend as Tm_2O_3 has a weak bond. As a result, bulk modulus also shows a reduction. However, the other elastic moduli show an increasing trend. This may be due to the increment of number of network bond per unit volume. Poisson's ratio is inversely proportional to average cross-link density. So, as $<n_c>$ is increasing, σ is decreasing. Ratio K_{bc}/K_e shows a decrement as well as the atomic ring size. Value of K_{bc}/K_e that is more than 1 indicates that the network has a large ring but become more closed as Tm_2O_3 is added and producing a rigid glass.

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