

PHYSICAL PROPERTIES OF BINARY TELLURITE GLASS SYSTEM

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ABSTRACT

The binary glass system of $(\text{TeO}_2)_x(\text{B}_2\text{O}_3)_{1-x}$ with $x = 60$ to 80 mol% were synthesized by rapid quenching method. Longitudinal and shear ultrasonic velocity were measured at room temperature and at 5 MHz frequency. Elastic properties, Poisson's ratio and micro hardness have been calculated from the measured density and ultrasonic velocity at room temperature. The transition temperature was also measured. The experimental results indicate that the elastic moduli of the binary glass system increase with TeO_2 content as the glass system become more rigid due to the mix former effect.

INTRODUCTION

Tellurite glasses are known to be an important amorphous system because they have low melting points yet lack the hygroscopic properties which limit the applications of phosphate and borate glasses and have commercial applications. Tellurite glass system is of scientific interest because of their low melting temperature, high refractive index, high dielectric constant and good infrared transmission [1]. The structure of TeO_2 based glasses is of special interest, the basic unit of glass with high TeO_2 content is an asymmetrical TeO_4 trigonal bipyramid with a lone pair electron in an equatorial position [2]. The doping of borotellurite glasses showed that appearance of distinct vibrational bands and a drastic change of the characteristic feature. The tetrahedral $[\text{BO}_4]$ units are gradually replaced by trigonal $[\text{BO}_3]$ units, the number of non bridging oxygen atoms increases and the coordination of the Te atom can be changed progressively and probably the formation of $[\text{TeO}_6]$ octahedral [3]. The aim of this work is to investigate the physical properties that consist of density, elastic properties and transition temperature of binary tellurite glass system. The results will be discussed with respect to the composition and structural changes.

EXPERIMENTAL METHOD

A series of binary tellurite glass system $\text{TeO}_2\text{-B}_2\text{O}_3$ was prepared with different mol percent of TeO_2 . The binary $\text{TeO}_2\text{-B}_2\text{O}_3$ glasses were synthesized by the method mentioned elsewhere [4]. The prepared samples were cut into required dimension for ultrasonic velocity measurement. For ultrasonic velocity measurement of the glass sample, MATEC MBS 8000 was used. All measurements were taken at 5 MHz frequency and at room temperature. The density of the glasses was determined by Archimedes method with acetone as buoyant liquid.

The glass transition temperature (T_g) were determined by the Differential Thermogravimetric Analysis (Setaram Instrumentation Labys, France) at heating rate of 20 K min^{-1} .

RESULT AND DISCUSSION

Figure 1 shows the x-ray diffraction pattern for binary tellurite glass. The results show no distinguishable peaks or sharp lines, but the pattern is hollow and gives a very broad hump. This type of diffraction pattern indicates that the samples are essentially amorphous rather than crystalline structure.

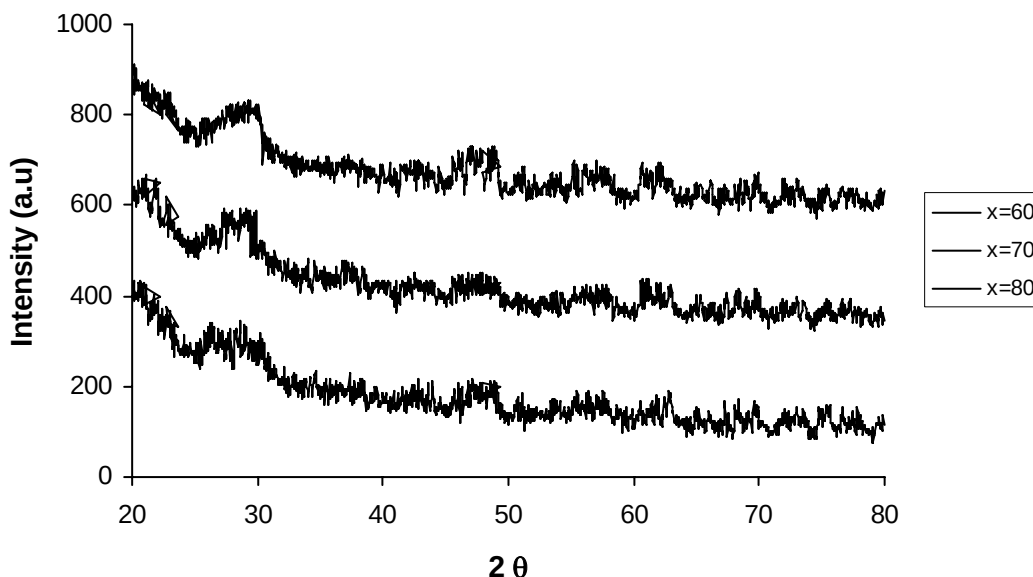


Figure 1: XRD spectrum of $(\text{TeO}_2)_x(\text{B}_2\text{O}_3)_{1-x}$ glasses

The density and molar volume of binary tellurite are plotted together in Figure 2. The density of B_2O_3 - TeO_2 glasses increases with the addition of TeO_2 . The substitution of TeO_2 with high atomic weight (159.5988) for B_2O_3 with low atomic weight (69.6202) may lead to an increase in density as the TeO_2 content increases as shown in Figure 2. The molar volume increases with an increase in TeO_2 content also. Generally, the density and the molar volume show opposite behaviour but in this work it is not. This anomalous behaviour was shown in a study by Rajendran *et al.* [5] and Saddeek and Abdul El-Latif. [6]. The increase in molar volume as a results of the creation of non-bridging oxygens (NBO), which break the bonds of borate and then spaces into the network increase [6]. The observed increase in molar volume may be due to an increase in the bond length or inter-atomic spacing between the atoms and the tellurium atoms space out into the network. The values of molar volume lie in the same range as that of tellurite glasses reported by El-Mallawany [7].

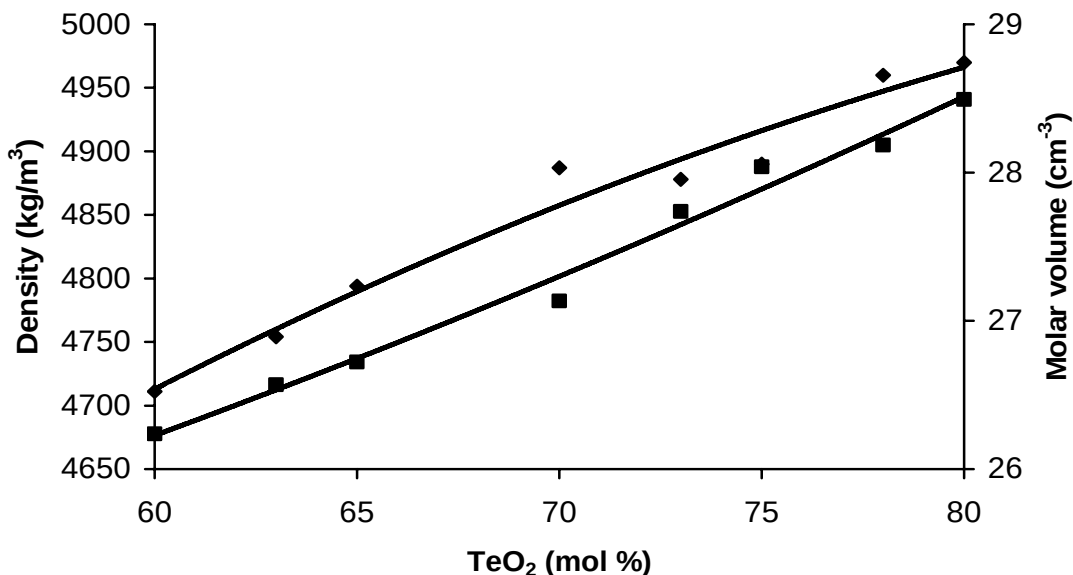


Figure 2: Density and molar volume of $(\text{TeO}_2)_x(\text{B}_2\text{O}_3)_{1-x}$ glasses

Table 1 shows both longitudinal (V_L) and transverse (V_S) velocities for $(\text{TeO}_2)_x(\text{B}_2\text{O}_3)_{1-x}$. It is clear that both ultrasonic velocities increasing with increasing TeO_2 content. The continuous increase in ultrasonic velocities is due to the increase in rigidity. According to Sekiya *et al.* [8], the structure of the B_2O_3 - TeO_2 glasses involves the conversion of BO_3 triangle to a BO_4 tetrahedron which is concurrent with the formation of a TeO_3 trigonal pyramid and this cooperative structural change plays an important role in glass formation. The observed value of the ultrasonic velocity in this binary tellurite system indicates that there is a substantial change in the glass structure. This change may be attributed to the increase in the rigidity, the packing density is nearly constant that is the non-bridging oxygen (NBO) are transformed into bridging oxygen (BO), therefore the ultrasonic velocity increases.

Table 1 compiles the longitudinal modulus (L), shear modulus (G), Young's modulus (E), bulk modulus (K), Poisson's ratio (σ) and microhardness (H). The elastic moduli at room temperature, Poisson's ratio and microhardness were calculated using equations as mentioned elsewhere [4]. In this study, the elastic moduli of binary tellurite system increase with the increase in TeO_2 content, as shown in Figure 3. This increase is attributed to strengthening of the structure with the addition of TeO_2 . As more TeO_2 is added more bridging oxygen (BO) are created [9]. The increase in elastic moduli is due to an increase in rigidity of glass samples. The increase in rigidity may be due to the stability of boron-oxygen structural fragments in $\text{BO}_{3/2}$ - TeO_2 glasses that is the stable electrostatic bridging oxygen atoms of Te-O-B and B-O-B linkages [8]. In the borotellurite glasses, TeO_4 units and BO_4 units have a strong tendency to link with each other to form $\text{BTeO}_{3.5}$ units, which results in a higher connectivity in the glass network and thus leads to a higher transition temperature [10]. Thus formation of a more rigid

and highly cross-linked network results in a tightly packed glass network.

Table1: Density, molar volume, ultrasonic velocity, elastic moduli and microhardness of $(\text{TeO}_2)_x (\text{B}_2\text{O}_3)_{1-x}$ glasses at room temperature

Mol%, x	60	63	65	70	73	75	78	80
Density, ρ (kgm^{-3})	4711	4754	4794	4887	4878	4890	4960	4970
Molar Volume (cm^3/mol)	26.24	26.57	26.72	27.13	27.74	28.04	28.19	28.49
Longitudinal Velocity, V_L (ms^{-1})	3467	3471	3581	3608	3692	3700	3800	3900
Shear Velocity, V_s (ms^{-1})	1981	2068	2086	2185	2206	2260	2300	2400
Longitudinal modulus, L (GPa)	56.63	57.28	61.48	63.62	66.49	66.94	71.62	75.59
Shear modulus, G (GPa)	18.49	20.33	20.86	23.33	23.74	24.98	26.24	28.63
Bulk Modulus, K (GPa)	31.98	30.17	33.66	32.51	34.84	33.64	36.64	37.42
Young's Modulus, E (GPa)	46.50	49.80	51.87	56.48	58.03	60.06	63.55	68.43
Poisson's Ratio, σ	0.2576	0.2248	0.2432	0.2104	0.2223	0.2024	0.2109	0.19524
Microhardness (GPa)	2.99	3.73	3.57	4.50	4.39	4.96	5.06	5.82
Transition Temperature ($^{\circ}\text{C}$)	356.99	357.20	356.02	354.74	355.34	355.75	356.49	356.04

The increase in microhardness is ascribed to the increase in bond strength of the glassy matrix [11]. This would result in an increasing in compactness of the glass network as TeO_2 increases. The change in microhardness reflects increasing connectivity of the glass network due to increasing concentration of the Te-O bonds. The increasing of bonds of type Te-O-Te, B-O-B and Te-O-B in the borotellurite glass system [8] will increase the average cross-link density in the glasses, which causes an increase in microhardness [12]. This can be seen in Figure 4, the microhardness increases with TeO_2 content.

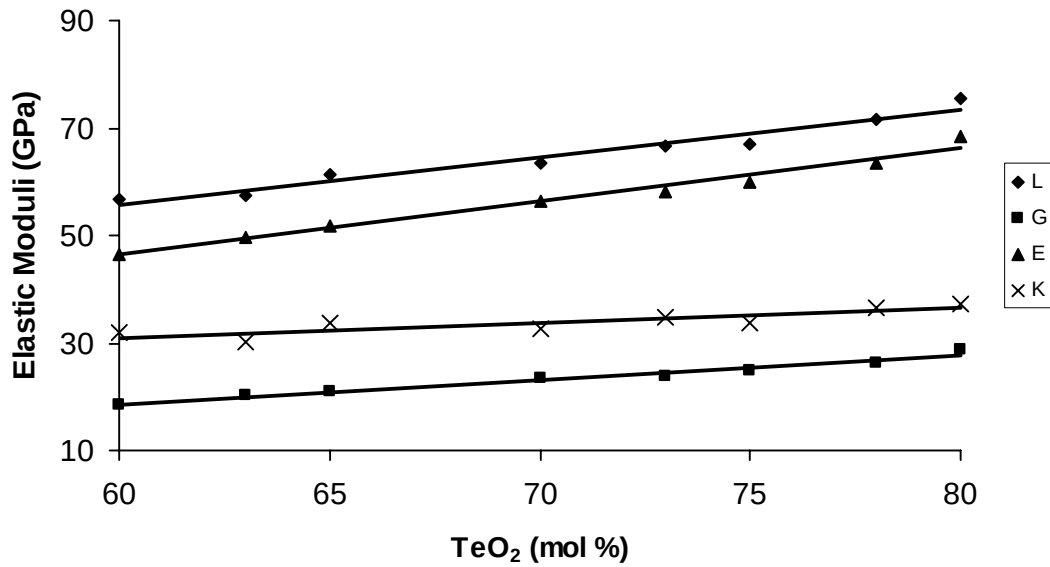


Figure 3: Elastic moduli of $(\text{TeO}_2)_x (\text{B}_2\text{O}_3)_{1-x}$ glasses

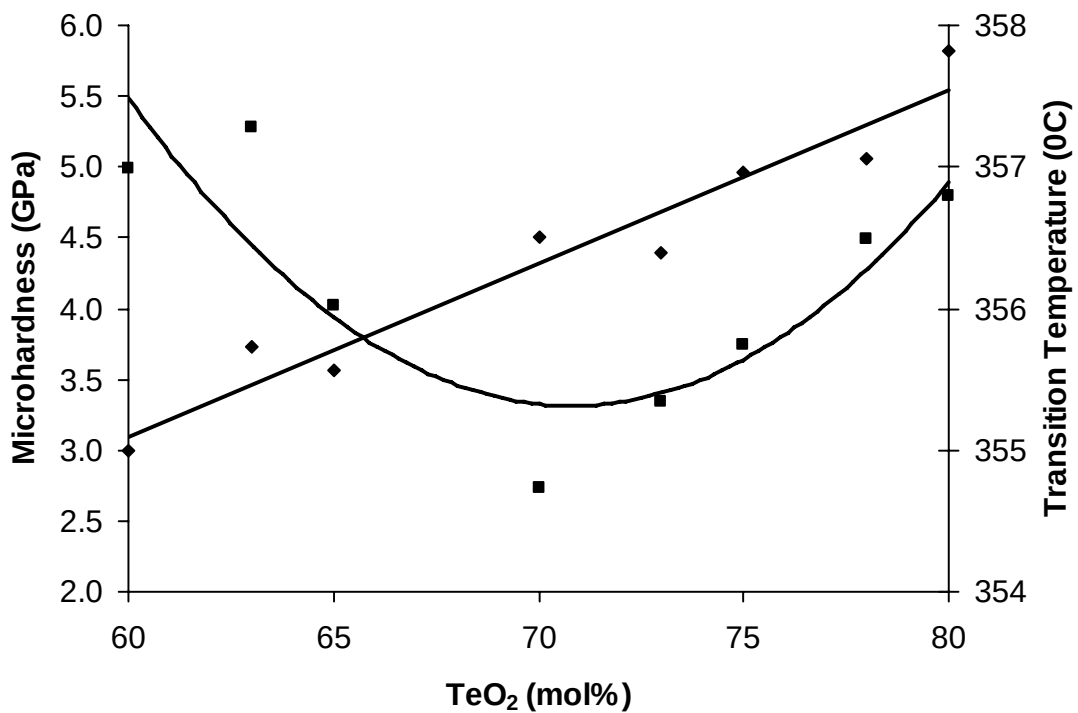


Figure 4: Microhardness and transition temperature of $(\text{TeO}_2)_x (\text{B}_2\text{O}_3)_{1-x}$ glasses

Figure 4 shows glass transition temperature for binary tellurite glass, at $x=63$ mol% the T_g value increases due to the conversion of BO_3 to BO_4 and TeO_4 to TeO_3 . Further addition of TeO_2 , in this region the break down of TeO_2 structure occurs by converting TeO_4 to TeO_3 . Although BO_4 units are introduced and their concentration is increasing, the net effect is weakening the structure and it pushes down the T_g value to some extent ($x=70$ mol%). At $x=70$ mol%, TeO_2 would generate more BO_4 units along with BO_3 units that creates a three dimensional network which permeate the glass structure. It is likely that the interpenetration of tellurite and borate network pushes up the T_g value ($x=78$ mol%). Above this the BO_4 units decrease the network strengthening influence of the permeating TeO_2 network wanes and the strength of the glass structure decreases; this can be seen at $x=80$ mol% as the T_g value decreases

Poisson's ratio for binary tellurite decreases when TeO_2 content increases as shown in Table 1. The decreasing value of Poisson's ratio is due to the change of the coordination number of borate atom with the increase TeO_2 content [13]. Addition of TeO_2 in place of boron oxide in the TeO_2 - B_2O_3 glasses results in an increase in the three-dimensional linkage due to the transformation of three-fold-coordinated borons (BO_3) into four-fold-coordinated ones (BO_4).

CONCLUSIONS

Binary TeO_2 - B_2O_3 glass system was successfully synthesized. The density increases with increasing Te_2O content. This is due to low atomic weight of B_2O_3 is replaced with high atomic weight Te_2O . The molar volume increases due to the formation of NBOs, which increases the distances between the structural groups of the glass system, and hence the packing density decreases. The elastic moduli, transition temperature and micro hardness increase while Poisson's ratio shows a slight decreasing trend. This is attributed to the progressive transformation of rigid glass structure due to mix former effect of tellurite and borate glass system.

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