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Synthesis and Elastic Behaviour of Borate Glass Doped with High Tellurite Content

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Abstract: A systematic series of quality binary glass system of (x)TeO_2)-(1-x)B_2O_3 with x = 60 to 80 (wt. %) were successfully synthesized by the rapid quenching method. The densities of each glass samples were determined using Archimedes method with acetone as a floatation medium. The molar volume have been estimated and analyzed for borate glasses doped with tellurite. Ultrasonics methods have been used to study the elastic properties of TeO_2.B_2O_3 glasses where the sound wave velocities have been measured in each glass samples at a frequency of 15 MHz and at room temperature. The velocities, both longitudinal and transverse, increase linearly with increasing of TeO_2 content in a borate glass network. Their elastic moduli such as longitudinal, Young's, bulk and shear modulus have been calculated as a function of TeO_2 concentration. Poisson's ratio and Debye temperature were also found to increase nonlinearly with TeO_2 concentration. The glass transition temperature were determined by the differential thermogravimetric analysis at heating rate of 20 K min^{-1}. However the glass transition temperature (T_g) slowly decrease as more tellurite is added into the borate glass network.

Key words: Borate, telurrite, glass, elastic properties, thermal behaviour

INTRODUCTION

Ultrasonic technique is a versatile tool for investigating the changes in microstructure, deformation process and mechanical properties of materials[1,2]. It is due to the fact that, the ultrasonic waves are closely related with the elastic and inelastic properties of the materials. The propagation of ultrasonic waves in solids provides important information regarding the atomic and/or molecular motion in materials. The velocity of ultrasonic waves and the elastic properties are particularly suitable parameters for characterizing glasses as a function of their composition. Some information about both the microstructure and elastic properties through the behaviour of the network and the modifier can be obtained. Furthermore the elastic measurement yields information concerning the forces that are operative between the atoms or ions comprising solid. This is fundamentally important in interpreting and understanding the nature of bonding in the solid state materials[3].

Tellurite glasses are considered as a new type of non-crystalline materials with lots of applications over a wide range of composition, temperatures and frequencies. The application of tellurite glasses in industries such as electric, optical, electronic and other fields are immense due to their good semiconducting properties, high densities, chemical durability, electrical conductivity, good infrared transmission capability, high dielectric constant, high refractive indices and stable and low melting points[4-6]. The absence of hygroscopic properties of these tellurite glasses is an advantage as compared with those of borate and phosphate glasses.

The tellurium oxide (TeO_2) itself is a conditional glass former and forms glass only with a modifier such as alkaline, alkaline earth metal and transitional metal oxides or other glass former. In a binary tellurite glasses, the basic structural unit of TeO_4 is trigonal bipyramid (TBP) with lone pair of electrons and the structural units take the Te-O-Te bond for glass formation[7]. Tellurite borate glasses have been extensively studied over the years to elucidate the nature and relative concentration of various borate units constituting the glass network[6]. In contrast, the ability of boron to exist in three and four oxygen coordinated environments and the high strengths of covalent B-O bonds enables borates to form stable glasses.

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There have been studies reported on several binary alkali borate glasses which show that there is a correlation between elastic properties and borate glass structure[8,9]. So far, the elastic properties of various borate glasses have also been reported[10-12], where their elastic properties have been discussed in terms of boron coordination. The main objective of the present research is to study the elastic and thermal behaviour of the borate glass containing high TeO_2 content.

MATERIALS AND METHODS

The binary $(x)TeO_2$-$(1-x)B_2O_3$ glasses were prepared by mixing together specific weights of tellurium dioxide (Aldrich 99.5%) and boron oxide B_2O_3 (Alfa Aesar, 97.5%), in a closed alumina crucible. The x percentage was 60, 63, 65, 70, 73, 75, 78, 80 wt.%. Appropriate amounts of powder chemical were weighed and poured into a crucible. The crucible was covered with a lid and then put inside an electric furnace set at 400°C. The mixture were kept at 400°C for a period of 30 min, the crucible was then transferred to a second furnace for 60 min at 800°C. The melt was then poured in a stainless steel cylindrical shaped split mould which had been preheated and then the sample was annealed at 350°C which is below their glass transition temperature. The prepared samples were cut into required dimension for ultrasonic, thermal expansion and transition temperature measurement. Detailed of glass samples preparation is available elsewhere[13,14].

The density (ρ) of the glasses were determined by Archimedes method with acetone as buoyant liquid, while their molar volume was calculated from the molecular weight (M) and density (ρ)[13,14]. All the weights were measured with a digital balance with ±0.001 g standard error.

The glasses were checked by X-ray diffraction for their amorphous nature using X-ray diffractometer (model Rigaku DMAX-1C) by employing Cr-Ka_radiation. The X-ray diffractogram did not show any sharp peaks, a characteristic of amorphous nature.

For elastic measurements, samples were polished using a lapping tool and uniform parallel surfaces of the samples were achieved. Ultrasonic velocity measurements were carried out at a frequency of 10 MHz using x-cut and y-cut quartz transducers. A pulse superposition technique was employed using Ultrasonic Data Acquisition System (MATEC 8020, Matec Instruments, USA). Burnt honey was used as a bonding material between the glass samples and transducers. By measuring the thickness of the sample (d), longitudinal (V_l) and transverse (V_t) wave velocities were calculated using the relation, $V = 2d/t$, where, t is transit time taken as ultrasonic waves travel in the glass samples.

Glasses are isotropic solid materials and have only two independent elastic constants namely longitudinal modulus, ($L = \rho V_l^2$), and shear modulus, ($G = \rho V_t^2$) where, V_l and V_t are longitudinal and shear sound wave velocity respectively and ρ is the density of the present glass samples. The various elastic properties of the glasses, such as bulk modulus (K), Young's modulus (E), Poisson's ratio (σ) and the acoustic Debye temperature (T_D) were calculated using the standard relations[13,14].

The glass transition temperature (T_g) were determined by the differential thermogravimetric analysis (Setaram Instrumentation Labys DTA/6) at) at heating rate of 20 K min^{-1}.

RESULTS AND DISCUSSION

Density is useful physical parameter to explore the degree of structural compactness, modification of the geometrical configurations of the glass network, change in coordination and the variation of the dimensions of the interstitial holes[15]. The variation of density and molar volume of borate glass with high tellurite content is shown in Table 1. It can be seen from Fig.1 that the density and molar volume of those glasses increase monotonically with the increase of TeO_2 content which is not only due to the introduction of a high atomic weight element but also due to volume contraction. The variation of density with TeO_2 content can be explained by considering the structural changes occurring in the coordination of boron glass network. The structure of crystalline as well as amorphous B_2O_3 is made up of planar $[BO_{3/2}]0$ triangles[16].

In amorphous B_2O_3, most of these triangles are arranged into boroxyl rings in which three oxygens are part of the ring and three oxygens are outside the ring. These rings are randomly interconnected through loose $[BO_{3/2}]0$ units. Due to the addition of modifying TeO_2, the three coordinated triangle boron $[BO_{3/2}]0$ units are converted to four coordinated boron tetrahedral $[BO_{4/2}]^-$ and thus the network dimensionality and connectivity increases. This would lead to efficient packing and compactness in the structure[16]. This is also reflected in the variation of molar volume as more TeO_2 being added into the borate network.

Generally the presence of TeO_2 in a borate glass, makes it as a colored one and hence in the present glass system all the glasses are slightly yellow in color (glasses which contains equal amount of TeO_2). The existence of such coloring property in these glasses may influence over the insulation and optical transmission properties[17].

Table 1: Density, longitudinal and transverse wave velocities, Poisson's ratio (σ), microhardness (H) and fractal dimensionality (d=4G/B) of (x)TeO_2-(1-x) B_2O_3 glass systems at various composition. The pure TeO_2 glass data taken from (a) Lambson *et al.*[7] and (b) El-Mallawany[6] and are used for comparison

TeO_2 (wt.%)	Density (kg m^{-3})	Molar volume (cm^3 mol^{-1})	V_L(m sec^{-1})	V_S (m sec^{-1})	σ	H(GPa)	Transition temperature T_g (°C)	d
60	4710	26.24	3467	1981	0.258	2.987	356.99	2.313
63	4750	26.57	3471	2068	0.225	3.726	357.20	2.696
65	4760	26.72	3581	2086	0.243	3.546	356.02	2.479
70	4775	27.13	3608	2185	0.210	4.401	354.74	2.871
73	4787	27.74	3692	2206	0.222	4.312	355.34	2.725
75	4890	28.03	3679	2231	0.209	4.719	355.75	2.886
78	4960	28.19	3609	2130	0.233	4.009	356.49	2.602
80	4970	28.49	3713	2241	0.213	4.767	353.04	2.833
Pure TeO_2	5,105[a]		3403	2007			322[b]	

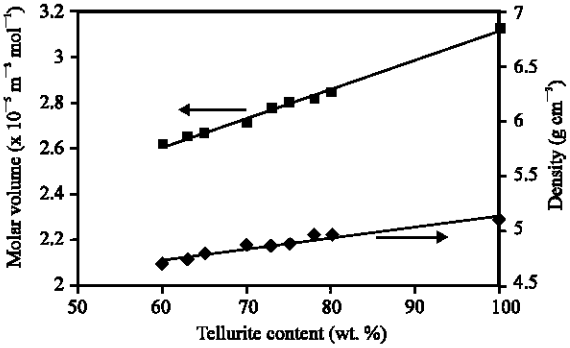

Fig. 1: Dependence of the density and molar volume of the glass system TeO_2-B_2O_3 on the tellurite content. Data of pure TeO_2 glass (100 wt.%) taken from Lambson *et al.*[7] is used for comparison

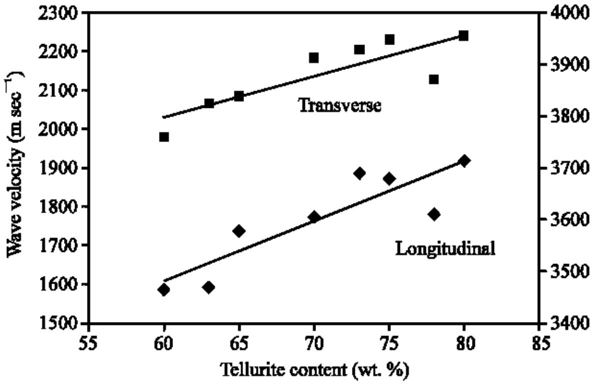

Fig. 2: Longitudinal and transverse wave velocities at room temperature in TeO_2-B_2O_3 glass system

As seen from Table 1 that the density increases from 4710 to 4970 kg m^{-3} and the molar volume increases from 2.624 to 2.849 x 10^{-5} m^3 mol^{-1}. Generally the density and the molar volume show opposite behaviour but in this study the behaviour is not opposite to each other. The increase in both of the molar and the density is attributed to changes occurred in the volume concentration of BO_3 units and the density of the glasses depends on the compactness of the structural units. The same behaviour has been found by Sidkey[18] and El-Adawy[19]. The volume increases rapidly with TeO_2 addition because of the effect of conversion B_3 to B_4 and brings about a change in structure, from linear (2 covalent linkages) to a 3-dimension (4 covalent linkages). In the case of tellurite glass, the glass structure is mainly composed of TeO_4 trigonal pyramids and the addition of other oxides results in structural changes to the TeO_3 trigonal pyramid[20].

The elastic moduli are proportional to the square of velocity and a plot of sound velocities vs. composition is indicative of relative structure. The compositional dependence of longitudinal (V_l) and transverse (V_t) sound velocities are shown in Fig. 2. While Fig. 3 shows the variation of elastic moduli as a function of tellurite content. As can be seen from Fig. 2 and 3, both (V_l), (V_t) and elastic moduli of longitudinal modulus (L), shear modulus (G), bulk modulus (K) and Young's modulus (E) increase with the increase of tellurite content over the entire composition studied.

This variation of ultrasonic wave velocities and elastic moduli can be explained on the basis of the structural consideration of borate network. As pointed out in the earlier section, the vitreous B_2O_3 consists of planar $[BO_{3/2}]0$ triangles[16]. The addition of tellurite into B_2O_3 network creates $[BO_{4/2}]^-$ units. This leads to increase in the network dimensionality and connectivity. Hence, both velocities and elastic moduli increase with the increase of TeO_2 content.

Glass is considered as elastic substance and, thus, can be characterized through a modulus of elasticity. This modulus increases as the lengthening at a certain applied stress. That will be the case if the glass structure is rigid and therefore contains the fewest possible non bridging oxygen. When an oxide is introduced to B_2O_3, the strengthen of the structure depends on the field strength of the action. The relatively open structure of B_2O_3 glass makes its modulus of elasticity low. With increasing TeO_2 content in the binary borate glass, the structure becomes

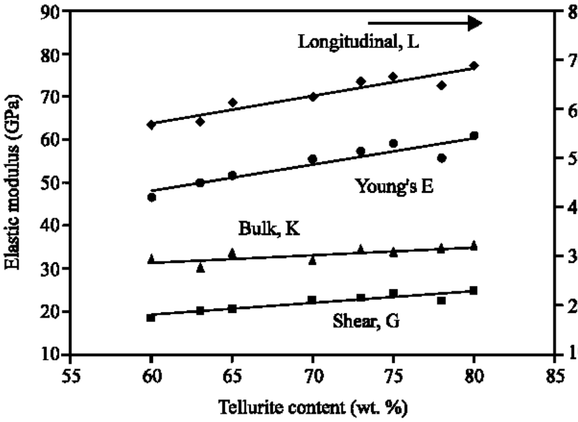

Fig. 3: Variation of the elastic moduli of TeO_2-B_2O_3 glass systems with tellurite composition

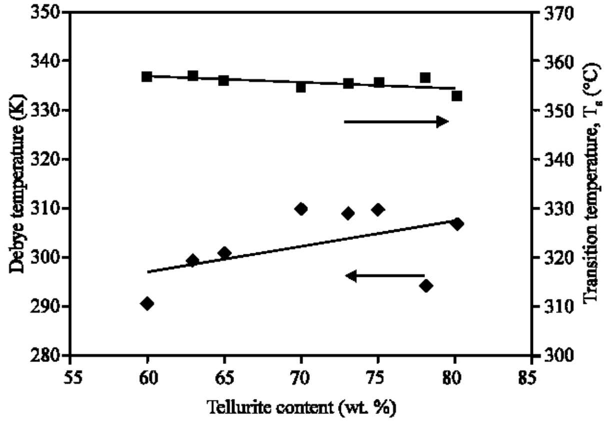

Fig. 4: The Debye temperature and glass transition temperature (T_g) of TeO_2-B_2O_3 glass systems at various tellurite composition

more rigid and the modulus of elasticity increases. This increase is very pronounced and according to Massot[21], reaches the maximum value when the number of B atoms is the coordination number 4 has its maximum. It may also be noted from Fig. 3 that the rate of change of elastic moduli is more pronounced in longitudinal modulus (L) and least in case of shear modulus (G). This indicates resistance to deformation and it is most probably due to presence of large number of covalent bonds[22, 23].

Young's modulus (E) is the ratio of the linear stress to the linear strain and is related to the bonding strength[1,5]. The Young's modulus is not only dependent on the interatomic bond strength of constituent atoms, but also depends on the packing state. The increasing of Young's modulus (E) for TeO_2-B_2O_3 glasses suggests that the addition of TeO_2 into the network strengthens the overall atomic bond strength.

Bulk modulus (K) is the ratio of the pressure to the decrease in volume per unit volume which can be derived most easily from the glass structure. The B_2O_3 glass posses an open structure characterized by many open spaces. The addition of TeO_2 will occupy such spaces and this should leads to an increase in bulk modulus. With low TeO_2 contents, the bulk modulus is small since many open spaces are present which will be filled most quickly by the large Te+ ions (ion radius of Te is 0.221 nm) so that the bulk modulus increases. With higher TeO_2 contents, the ability for deformation of the cations becomes decisive. This is clear from Fig. 3, which shows the relation between bulk modulus and TeO_2 content. The overall result for the bulk modulus of these glasses is comparable with those of pure TeO_2 glass (31.7 GPa)[7].

As already known, pure B_2O_3 exists in planner three-fold coordination. The addition of network modifier (TeO_2 in this case) produces four-fold coordinated boron by cross linking the planar triangles and would be expected to tighten and strengthen the network. This tetrahedral structure gives B_2O_3 maximum rigidity and increase in velocity indicating that the network former becomes rigid and resists deformation.

Microhardness (H) of borate tellurite glasses as given in Table 1, was calculated according to the equation given by Kodama[8] in the form; $H = (1-2\sigma) E/6 (1+\sigma)$ where, σ is Poisson's ratio and E is Young's modulus. The value shows the same features as that observed in Fig. 2 for the sound velocity.

Poisson's ratio, σ is defined as the ratio of the lateral contraction per unit length to the longitudinal extension per unit length, at a linear stress. The compositional dependence of Poisson's ratio as a function of TeO_2 content is given in Table 1. Poisson's ratio has also been discussed in terms of the dimensionality of glass network and it is observed that the Poisson's ratio for a three dimensional network is less than that of a two dimensional structure, which in turn is less than that of a one dimensional structure. This has been attributed to the fact that the concentration of bonds resisting a transverse deformation decreases in that order[23]. As it can be seen from Table 1, the Poisson's ratio is found to decrease with an increase of tellurite content. The decrease in Poisson's ratio suggests formation of a strong B-O-Te linkages in place of weaker B-O-B linkages. Furthermore, the values of Poisson's ratio are believed that of covalently bonded structure.

Debye temperature, θ_a represents the temperature at which nearly all modes of vibrations in a solid are excited and its increase implies an increase in the rigidity of the glass. The compositional dependence of Debye temperature as a function of tellurite content is shown in Fig. 4. The increasing trend in TeO_2-B_2O_3 glasses means that the glasses have become more rigid as more TeO_2 is added and this agrees well with the internal structures that we have discussed. The gradual increase of Debye temperature also suggests increase in the compactness in the structure leading to increase in mean sound velocity[23,24].

The transition temperature behaviour, as shown in Fig. 4, is behave nonlinearly where the Tg value decreases due to the conversion of BO_3 to BO_4 and TeO_4 to TeO_3. Further addition of TeO_2, in this region will break down TeO_2 structure by converting TeO_4 to TeO_3. Although BO_4 units are introduced and their concentration is increasing, the net effect is weakening structure and it pushes down the Tg value to some extent. But around 70 wt.% TeO_2 it would generate more BO_4 units which along with BO_3 units creates a 3-dimensional network which infuse the glass structure. It is likely that the inter-penetration of the tellurite and borate network pushes up the Tg to about 78 wt.%. Above this the BO_4 content drops, the network strengthening influence of the permeating TeO_2 network wanes and strength of the glass structure decrease[8], this can be seen as decreasing trend in glass transition.

CONCLUSIONS

Elastic properties and thermal studies of $(x)TeO_2$-$(1-x)B_2O_3$ glass system have been studied to ascertain the role of Te^{2+} ion in these glasses. The sound velocities, V_l and V_t, elastic properties and Debye temperature show increasing trend as more TeO_2 is being added into the borate glass network. The decrease in Poisson's ratio suggests formation of a strong B-O-Te linkages in place of weaker B-O-B linkages. The density and the molar volume increase with composition due to the compactness of the structure. The variation in transition temperature observed in these glasses is due to the conversion of BO_3 to BO_4 and TeO_4 to TeO_3.

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