

ULTRASONIC AND THERMAL PROPERTIES OF BORATE AND PHOSPHATE GLASSES DOPED WITH BISMUTH AND LEAD

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ABSTRACT

A systematic series of $(\text{B}_2\text{O}_3, \text{P}_2\text{O}_5)\text{-Bi}_2\text{O}_3\text{-PbO}$ glasses have been successfully prepared by using the rapid quenching technique where each oxides contents change for every series based on their weight percentage. Their amorphous natures were confirmed earlier by the X-ray diffraction technique. The experimental results show that the density of both glasses, determined by using the Archimedes' principle, increase with glass modifier content. This is due to the replacement of Bi_2O_3 and PbO in the borate and phosphate glassy networks. The molar volume for borate glass increase with addition of bismuth and lead oxides, however a reverse trend occurs for the phosphate glass. The longitudinal and shear ultrasound velocities, determined by the MBS 8000 system, of both lead bismuth borate and phosphate glasses show decreasing trend as more PbO and Bi_2O_3 are being added into the glass system. The increase in $\text{PbO}/\text{Bi}_2\text{O}_3$ content was probably related to the progressive increase in the concentration of non-bridging oxygen (NBOs). Thermal studies of the glass, using Labsys DTA - Setaram machine, show that values for glass transition temperature (T_g) is closely related to the chemical bond in the system. In lead bismuth borate glasses, the addition of more Pb^{2+} and Bi^{3+} will result in the ionic bond character became more dominant in the system and hence decreases the T_g of sample. However, in lead bismuth phosphate glasses, the addition of Pb^{2+} and Bi^{3+} not only failed to weaken the covalent character in P–O–P bonds, but strengthened it further which leads to an increment in T_g values.

INTRODUCTION

Bismuth borate glasses have been widely investigated showed some excellent optical properties, high refractive index, nonlinear optical behaviour and strong ultraviolet absorption (Chen *et al.*, 2003). Meanwhile, lead oxide based glass can be formed over a wide concentration. Moreover, PbO can enter the glass network both as a network modifier and also as a network former (Meera *et al.*, 1989). It was suggested that the addition of one or, more of metal oxides leads to dramatically improvement in the chemical durability of the phosphate glasses (Shih *et al.*, 1998). Proper selection of glass composition lead to phosphate glasses with good durability. Among the heavy metals, bismuth is the heaviest and the only non-toxic element.

El-Adawy and Moustafa (1999) have studied the variation of the elastic internal

energies of longitudinal and shear strains per unit mole of the $\text{Bi}_2\text{O}_3 - \text{B}_2\text{O}_3$ glasses. Rajendran *et al.* (2002) found that the increase values for both ultrasonic velocities and elastic moduli in the $\text{Bi}_2\text{O}_3 - \text{BaTiO}_3$ oxide glasses are related to an increase in cross linkage, thus, the rigidity of the network and hence increase in Debye temperature. Paul *et al.* (1997) found that the ultrasound velocity in the lead-phosphate glass, increased with the decrease of PbO content without any discontinuity at particular temperature.

Khanna *et al.* (2003) found the glass transition temperature increased while the density and longitudinal modulus decreased with melt ageing time for $\text{Bi}_2\text{O}_3 - \text{B}_2\text{O}_3$ glasses. It is known that the decrease of Bi_2O_3 concentration in bismuth borate glasses leads to a decrease in density and an increase in glass transition temperature. Becker (2003) also found an increase in glass transition temperature with the decrease in Bi_2O_3 content. Nitta *et al.* (2001) found that glasses with a bismuth oxide have lower T_g than usual silicate glasses and bismate glasses, known as materials with unique optical and thermal properties. The T_g of glass containing the same amount of alkaline oxide is almost the same regardless of type of alkaline element, and it is found that the amount of B_2O_3 in 10 mol% hardly affects T_g .

Phosphate based glasses in general, show low melting points, low glass transition temperatures and low softening temperature (Shih *et al.*, 1998). In ternary phosphate based glass, Franks *et al.* (2001) found that the T_g varied almost linearly with refractory material content and would increase T_g as more was incorporated into the glass. Guo and Chen (1996) also mentioned that many phosphate glasses exhibited a high thermal expansion coefficient and poor chemical durability, and an improved chemical durability was often accompanied by substantial decrease in thermal expansion. Guo and Chen (1996) in their recent investigation showed that a lead – barium – aluminium phosphate glass had a good chemical durability by allowing a high coefficient of thermal expansion.

Although ultrasonic studies on number of binary borate and phosphate have been performed by previous researchers, however, no such study has been done for ternary $\text{PbO} - \text{Bi}_2\text{O}_3 - \text{B}_2\text{O}_3$ and $\text{PbO} - \text{Bi}_2\text{O}_3 - \text{P}_2\text{O}_5$ glasses so far. The main objective of this research was to study the physical characteristics of lead bismuth borate and lead bismuth phosphate glasses. In order to achieve this, three major objectives have been designed as follow; to produce the borate and phosphate based glasses using conventional melt quenching technique, to characterize their ultrasonic wave velocities and to determine their glass transition temperature using DTA principle.

EXPERIMENTAL PROCEDURE

All batches of lead bismuth borate and lead bismuth phosphate glasses were prepared using bismuth (III) oxide, Bi_2O_3 (99.975%, Alfa Aesar), lead (II) oxide, PbO (99%, Strem Chemicals), boron oxide, B_2O_3 (99%, Acros Organics) and phosphorus (V) oxide, P_2O_5 (97%, HmbG Chemicals) and weighted using Weighfield Electronic Balancer (± 0.01 g). In the melting process, the porcelain crucible with the mixture was

transferred to another electric furnace, manufactured by Lindberg, Thermolyne and Bole, and kept at 1000°C. This process was kept for 60 minutes for lead bismuth borate and 45 minutes for lead bismuth phosphate. During this process, the crucible was slightly shaken using metal holder several times to ensure homogeneity and proper mixing.

After the melting process, each melt was quenched rapidly into cylindrical stainless steel split mould preheated at 350°C, to form glass rods at 2.0 cm height and 1.1 cm diameter. After casting, each glass was immediately transferred to an annealing furnace held at 400°C for 60 minutes for both lead bismuth borate and lead bismuth phosphate glass samples. The furnace was then switched off and the glasses were allowed to cool down to room temperature before its kept in dry box or desiccators.

The glass samples were cut using the Buehler Isomet low speed saw machine. The glass sample was then grinded using various grades of sand paper to get the parallel, smooth and clear surface for each glass samples. 20 samples for lead bismuth borate and 12 samples lead bismuth phosphate glasses have been successfully prepared. Figure 1 shows the composition of glass samples, where five samples for each series in lead bismuth borate and four samples for each series in lead bismuth phosphate.

All the glass samples were cut using Isomet Low Speed Saw machine to obtain 0.5 cm to 1.0 cm height samples. The ultrasonic wave propagation can be obtained by using the Matec Instruments MBS-8000 computer controlled ultrasonic test system. The Matec DSP system utilizes a high precision, high-resolution measurement technique, which calculates time of flight, velocity, attenuation and dispersion of ultrasonic waveforms automatically, at single or over a multiple frequencies (Sidek et al, 1996; 1998). The glass transition temperature was determined by using the Setaram Labsys DTA/DSC equipment. The Philips X'pert Model PW3020 X-ray Diffractometer was used to check the characteristic of amorphous or glass materials.

RESULTS AND DISCUSSION

Lead Bismuth Borate and Phosphate Glass Samples

Each series ternary lead bismuth borate and phosphate glass consisted of systematic decrease for weight percentage of B₂O₃ / P₂O₅, with different increase percentage for PbO and Bi₂O₃ as shown in Figure 1. All glass series were successfully prepared.

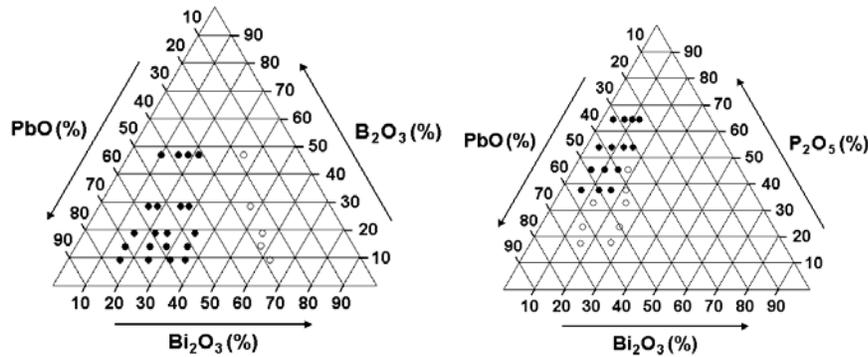


Figure 1: Composition of lead bismuth borate (left) and phosphate (right) glass samples and glass forming region. Glass are presented with solid point, and open circles for non-glass.

For these glass samples, one could observe a slight change in colour from colourless to yellowish as the PbO and Bi₂O₃ values were increased in the glassy networks. Bux (2003) found similar pattern with the increasing of Bi₂O₃ in his binary Bi₂O₃ – B₂O₃ glass system. Similar observation was also observed by Gressler (1989) and Azman (2000), where both found that an addition of PbO into the borate glass system gradually altered the colour of the glass from colourless to yellowish.

By referring Figure 1, it is notable that the lead bismuth borate system forms glasses in the wide range of PbO and Bi₂O₃ concentration compared to the phosphate system. It is clear that B₂O₃ which plays a role of network former enlarges the glass forming region (Nitta *et al.*, 2001). But at one point, when the compositions contained more Bi₂O₃ (> 40%) and less PbO (< 30%), a clear glass became difficult to obtained. At this stage, the samples are in the white colour and non-transparent. Based on this character, we assume that the samples produced already entered the ceramic forming region.

In the case of phosphate glasses, the primary network glass former is P₂O₅. The P₂O₅ provides the backbone of the glass structure, forming tetrahedra composed of one phosphorous ion surrounded by four oxygen ions. The sample produced with high P₂O₅ content (65.0%) were much easier to break and this weakness has been overcome with the introduction of PbO and Bi₂O₃ into the glass network. P₂O₅ itself that is very anhydrous, and readily reacts with water in the atmosphere. Also, in the compositions which contained less percentage of P₂O₅ (< 33%), it became difficult to produce clear samples with the addition of PbO and Bi₂O₃. Similar to borate system, at this point the sample obtained are in the white colour and non-transparent.

In general, all the phosphate glasses were of good quality, transparent, clear, bubble-free, and physically colourless. An introduction of lead and bismuth oxides into the phosphate glass system did not create any colour changing in the glass samples. Earlier works by Azman (2000) for the PbO – P₂O₅ glass system were also produced similar observation.

X-Ray Diffraction on Glass Samples

The XRD patterns of selected glass samples obtained are shown in Figure 2 for lead bismuth borate and phosphate glasses. All the selected quenched materials were found to show broad halo, which reflected the characteristic of amorphous or glass structure, obtained at around $2\theta \approx 30^\circ$ (Aksan *et al.*, 2000).

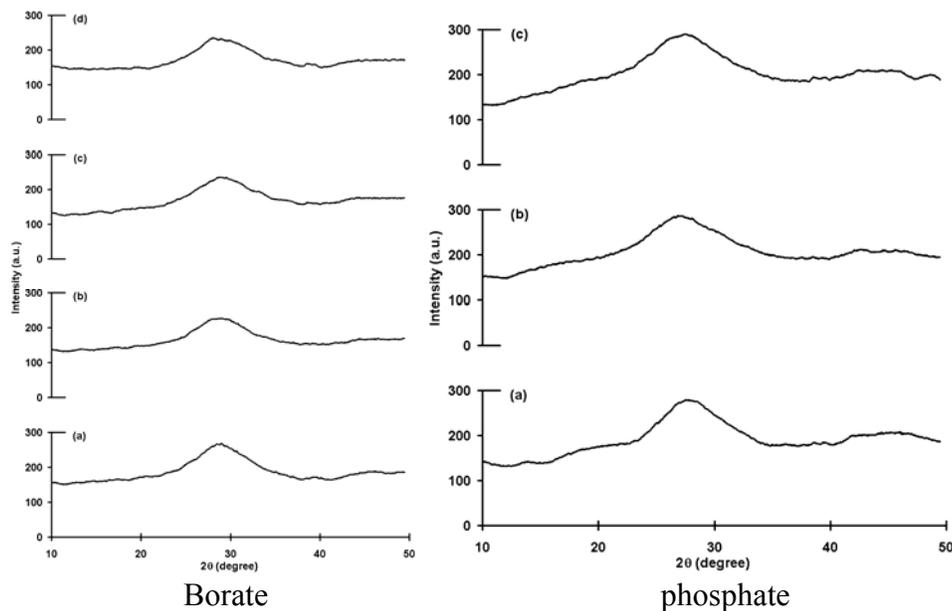


Figure 2: XRD patterns of lead bismuth borate glasses, (a) Glass sample A3, (b) Glass sample B3, (c) Glass sample C3 and (d) Glass sample D3, and for lead bismuth phosphate glasses, (a) Glass sample E3, (b) Glass sample F3 and (c) Glass sample G3.

The appearance of broad profile around $2\theta \approx 30^\circ$, also suggests that some short range order in the borate and phosphate glasses are preserved (Dayanand *et al.*, 1995). The absence of sharp, strongly diffracted beams in the X-ray diffraction patterns from glass indicated that there were no well defined planes in the structure on or around which the constituent atoms were regularly arranged.

Density and Molar Volume

The densities and molar volume (ρ and V_m , respectively) of lead bismuth borate and phosphate glasses are plotted in Figure 1 and Figure 2 respectively. The density of this ternary glass system showed a linear increase as PbO and Bi₂O₃ being added into the glass matrix. This behaviour was consistent for every series of glass with approximately 3.2% to 28.2% of increases in density and 2.8% to 13.3% increases for molar volume. The addition of Bi₂O₃ in the B₂O₃ network, increased the number of non-bridging

oxygen (NBO) atoms which in turn increased the density of glass, and this may be attributed to replacement of a low-density oxide (B_2O_3 , 2550 kg/m^3) by a high-density oxide (Bi_2O_3 , 8990 kg/m^3 and PbO , 9530 kg/m^3) (Saddeek, 2004). The increases in the density also consistent with the previous work on the bismuth borate glass system (Chowdari and Rong, 1996; Becker, 2003). The addition of PbO into the glass system caused the densities to increase and the increases indicated that the Pb^{2+} as a network modifier altered the structure of the glass by creating the NBOs in the network, so that the structure turns out to be more randomly oriented (Azman, 2000).

Meanwhile an increase in the molar volume may be attributed to an increase in the bond length or inter-atomic spacing between the atoms. The radius of Bi^{3+} (0.102 nm) is much greater than that of B^{3+} (0.020 nm) (Saddeek, 2004), and since the Pb^{2+} (0.120 nm) which also has greater radius than B^{3+} attributed to this situation. Saddeek (2004) also mentioned, generally the density and the molar volume of materials show opposite behaviour. However in this study, it is contrast and this discrepancy can be explained by assuming the increase in both of the molar volume and density is attributed to changes occurred in the volume concentration of BO_3 units (Yawale *et al.*, 1995).

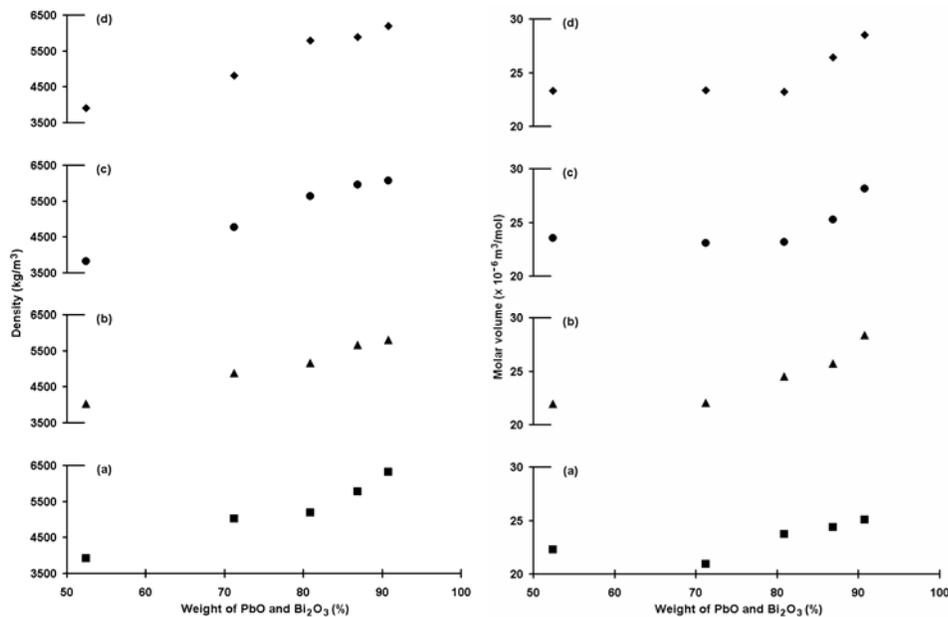


Figure 3: Density and molar volume of lead bismuth borate glasses, where (a) A1 – A5, (b) B1 – B5, (c) C1 – C5 and (d) D1 – D5.

The densities and molar volumes for every series in this ternary glass system are shown in Figure 4. From the result, it can be seen the increasing values of density with the

addition of PbO and Bi₂O₃. However the molar volumes were found to be different, where a decrement in values obtained. Both of these situations occurred for every series of glass in the system. As reported for the ternary lead bismuth borate glass system, the addition of PbO and Bi₂O₃ that consist of Pb²⁺ and Bi³⁺ will modify the glass structure by creating NBOs in the network, and this situation might occur in lead bismuth phosphate system.

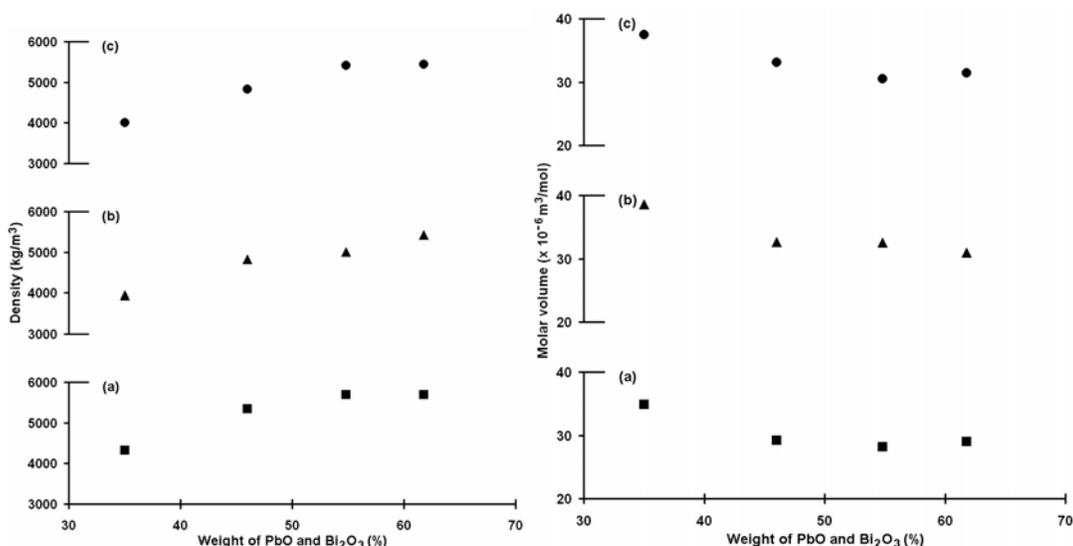


Figure 4: Density and molar volume of lead bismuth phosphate glasses, where (a) E1 – E4, (b) F1 – F4 and (c) G1 – G4.

The NBOs created were believed to alter the glass structure in a way that packing of the molecule becomes denser as more network modifier ions (in this case Pb²⁺ and Bi³⁺), attempt to occupy the interstices within the network (Low *et al.*, 1999). An increase of the density of the glasses accompanying the addition of Bi₂O₃ is probably caused to a change in cross-link density and coordination number of Bi³⁺ ions (El-Adawy and Moustafa, 1999). The results from this work are consistent with the studies done on the phosphate based glasses by Higazy and Bridge (1985), Paul *et al.* (1997) and Sidek *et al.* (1998).

Dayanand *et al.* (1996) suggested that Pb²⁺ ions in the PbO – P₂O₅ glass, occupied a position between P–O–P layers. This is why they have a direct influence of P=O bonds of P₂O₅ groups according to the scheme Pb²⁺–O=P⁵⁺. Under this interaction, the oxygen atom of the phosphoryl (P=O) group is included into the lead coordination polyhedron, and Dayanand *et al.* (1996) described it sequentially as shown in Figure 5. The probable role of PbO as network modifier in lead phosphate glasses is depicted in these structures. Thus, the inclusion of an oxygen atom into the lead sphere leads to an elongation of the affected P=O bonds.

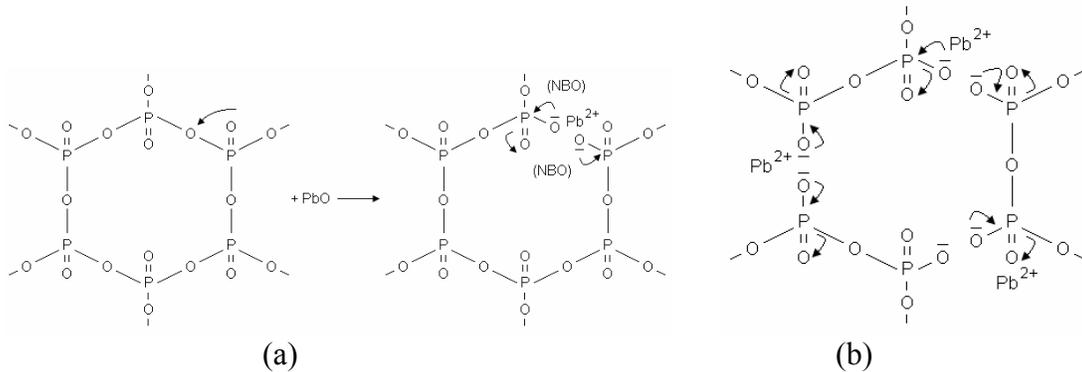


Figure 5: (a) The probable structural mechanism by which PbO enters into the P₂O₅ network and creates additional NBOs in the phosphate tetrahedral by leaving the P–O–P links, (b): Increase in the number of additional NBOs as the PbO content increase (after Dayanand *et al.*, 1996).

Meanwhile for the molar volume values, it shows a reverse trend from the glass density. In general, the density and the molar volume show opposite behaviour (Saddeek, 2004). The decrement trend of molar volume was due to the reduction of atomic molar volume as the network modifier ions (Pb²⁺ and Bi³⁺), interrupt the network structure by insertion of NBOs with essentially non-directed polar bonding to cations (Low *et al.*, 1999).

Velocity of Wave Propagation

The measured longitudinal and shear velocities (V_L and V_s , respectively) for lead bismuth borate glass are depicted in Figure 6. An interesting feature occurs that there is a decrease in values for both wave velocities, and this happen for every series of glass. The decrease of ultrasonic velocity linearly with the increasing of Bi₂O₃, indicating that Bi₂O₃ plays a dominant role in the velocity (Yawale *et al.*, 1995). An addition of more Bi₂O₃ in glass interstices causes more ions being open up in the network. Thus, weakening of the glass structure or reduction in the rigidity of the network takes places. As consequences, both velocities V_L and V_s decrease with the addition of heavy metal oxide (HMO).

The observed higher values in velocity at low Bi₂O₃ content and low values in velocity at high Bi₂O₃ content confirm a substantial change in glass structure. The Bi³⁺ cations are incorporated in the glass network as [BiO₆] octahedral units, on the expense of the Bi³⁺ cation which is incorporated as BO₃ and then converted in to BO₄, namely Bi₂O₃ has higher number of network bonds. The stretching force constant for Bi₂O₃ (216 N/m) is less than that for B₂O₃ (450.7 N/m for BO₃ and 401.2 N/m for BO₄) and the molar volume of Bi₂O₃ is $52.4 \times 10^{-6} \text{ m}^3/\text{mol}$ which is larger than that of B₂O₃, which is $27.3 \times 10^{-6} \text{ m}^3/\text{mol}$. The further addition of Bi₂O₃ causes more and more discontinuity and, hence, a decrease in rigidity and velocity results (Saddeek, 2004).

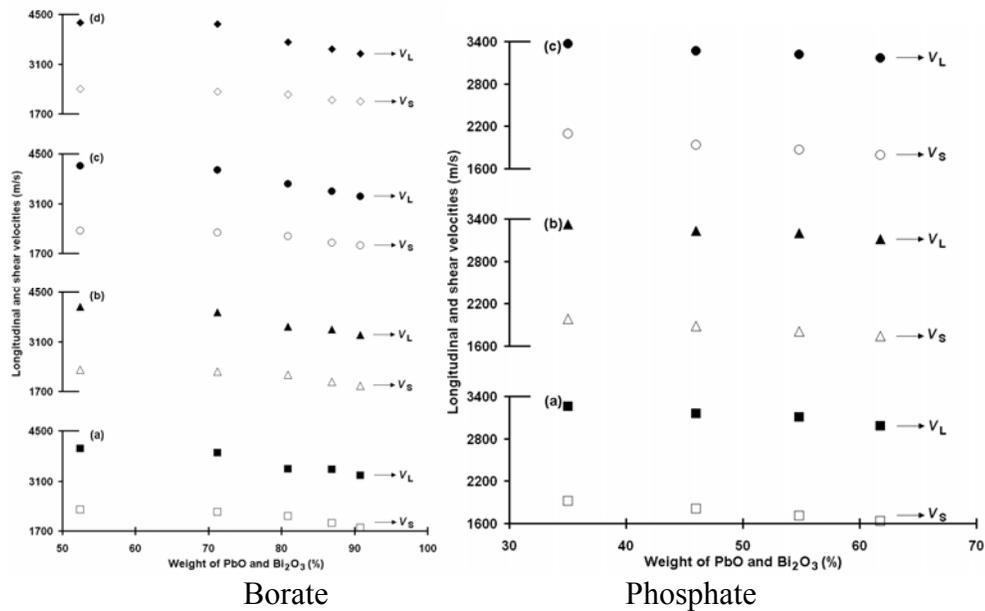


Figure 6: Longitudinal and shear velocities of lead bismuth borate glasses, where (a) A1 – A5, (b) B1 – B5, (c) C1 – C5 and (d) D1 – D5., and for lead bismuth phosphate glasses, where (a) E1 – E4, (b) F1 – F4 and (c) G1 – G4.

A decrease in velocity was also obtained by Bux (2003), in his research on $\text{Bi}_2\text{O}_3 - \text{B}_2\text{O}_3$ glass system. Meanwhile, the addition of PbO to the borate glass system will decrease both of velocities and cause the glass properties to be changed (Azman, 1997). To interpret the compositional dependence of the wave propagation in the lead borate glasses, one should consider the effect of bond strength, packing density, coordination number and crosslinking in the glass, where those parameters play important roles in determination of the structural changes.

As shown in Figure 6, the longitudinal and shear velocities of lead bismuth phosphate glasses decrease as more PbO and Bi_2O_3 added into the glass system and this happen for every series of glass. The increase in PbO content was probably related to the progressive increase in the concentration of NBOs (Dayanand, 1994). Therefore, the structures of the binary $\text{PbO} - \text{P}_2\text{O}_5$ glasses are weakened with the increase in mole fraction of PbO in the glasses as a result of the increasing NBOs (Sidek *et al.*, 1998). Since the addition of glass modifier (PbO and Bi_2O_3) produced the increment in density and decrement in ultrasonic velocity, where both of them related this situation with the increment in NBOs, confirms a substantial change in glass structure like what happen in lead bismuth borate glass system.

Glass Transition Temperature

Figure 7, clearly shows that the transition temperature of every series decreased as PbO and Bi₂O₃ content increased. This is mainly due to the addition Bi₂O₃ which weakens the bond between each atom in sample (increases the number of NBOs atoms). The bond getting easier to break and hence the T_g of the sample decreased. It was found that approximately 1.06% to 9.74% and 1.67% to 5.65% decreased between each samples in both series.

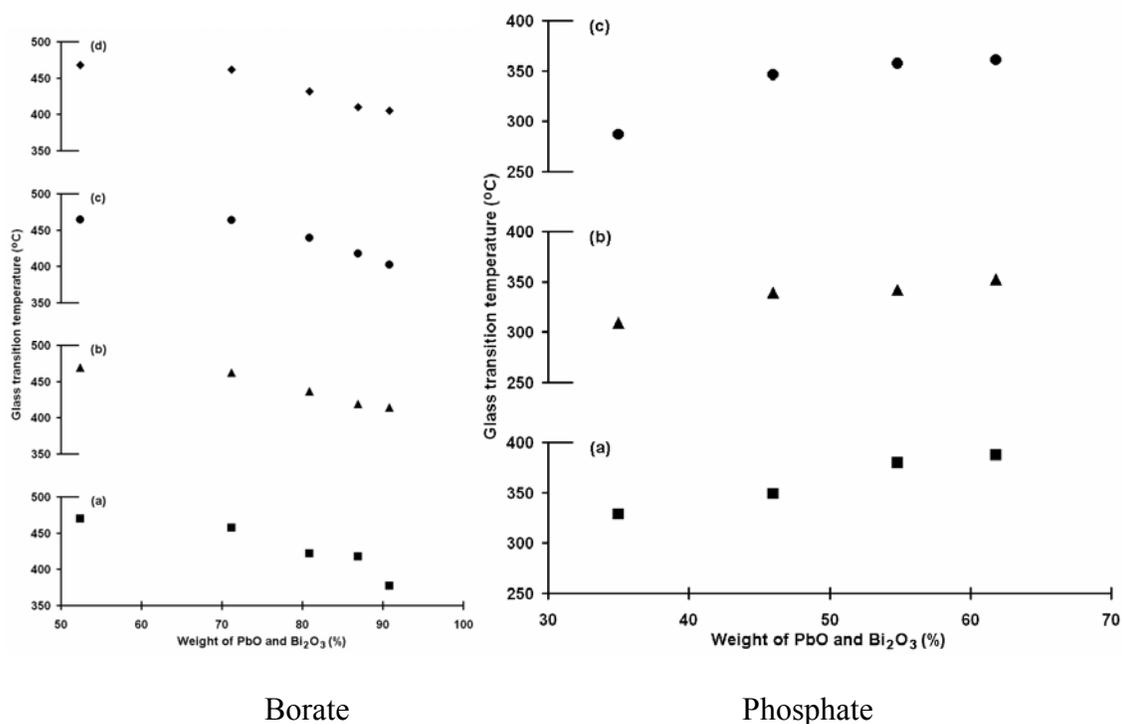
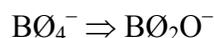


Figure 7: Glass transition temperature of lead bismuth borate glasses, where (a) A1 – A5, (b) B1 – B5, (c) C1 – C5 and (d) D1 – D5, and for lead bismuth phosphate glasses, where (a) E1 – E4, (b) F1 – F4 and (c) G1 – G4.

The current finding is comparable to the thermal properties of the Bi₂O₃ – B₂O₃ (Becker, 2003); the variation in glass transition temperature with glass composition is caused by the subsequent formation of dipentaborate units with increasing amounts of Bi₂O₃. The decrease of Bi₂O₃ concentration in borate glasses lead to a decrease in density and an increase in glass transition temperature (Khanna *et al.*, 2003). It was suggested that the following structural transformations (Huang *et al.*, 1993):



where \emptyset represents a bridging oxygen and O^- a non-bridging oxygen, take place slowly in the borate melt and are responsible for the change in various glass properties. $B\emptyset_2O^-$

units are estimated to have volume about 1.70 times more than that of $B\text{O}_4^-$ unit by the NMR studies carried out by Karki *et al.* (1987). Meanwhile, if the breaking up of boron tetrahedral units, $[B\text{O}_4]^-$, into a triangular boron units, containing two bridging and one NBO, $B\text{O}_2\text{O}^-$, had been the only transformation occurring in the melt, the glass transition temperature should have decreased drastically (Martin and Angell, 1984).

It was also found that, Li^+ or Na^+ were stabilized around tetrahedral boron units, $[B\text{O}_4]^-$, while Pb^{2+} , Bi^{3+} and Sn^{2+} were stabilized around $B\text{O}_2\text{O}^-$ (Khanna *et al.*, 2003). This has been supported by NMR and X-ray photoelectron spectroscopic studies on $\text{SnO} - \text{B}_2\text{O}_3$ glasses by Hayashi *et al.*, (2002). Thus, tetrahedral boron unit are inherently unstable in the presence of ions like Pb^{2+} and Bi^{3+} and break into much larger metaborate triangular unit, $B\text{O}_2\text{O}^-$, which in result creating more NBOs.

As shown in Figure 7, the glass transition temperature for this phosphate system increased with the increasing of PbO and Bi_2O_3 content. As an example, for E1 to E4 and F1 to F4 glass samples, the temperature increased from 328.59°C to 387.70°C and 309.19°C to 352.42°C which represents 17.99% and 13.98% of increases for both series. Also, it was found approximately 2.07% to 8.91% and 0.92% to 9.74% of increases between each sample in both E and F glass series.

Beside that, the data also indicated that the temperature were found to be low than borate glass system. Phosphate glasses exhibit very important physical properties such low melting temperature, high thermal expansion coefficient, low glass transition temperature, and low softening temperature. The decrease in the glass transition temperature with lead content can be explained by weaker cation crosslinking between the different phosphate chains. Unfortunately, this cannot be applied in the current studies. The result obtained, indicated that the Bi_2O_3 substance played a dominant role to represent a trend for T_g in lead bismuth phosphate glass system and the glass transition temperature were very sensitive to glass composition where it jumped sharply with decreasing of P_2O_5 content. This is probably due to the field strength of the bismuth cation is higher than that of the lead cation, thus, providing a stronger crosslinking between phosphate chain, which in turn increases the T_g (Shih *et al.*, 1998).

CONCLUSIONS

Two types of new ternary bismuth based glass samples were successfully prepared and their glassy natures were determined using the XRD method. All the selected samples clearly show the characteristic of amorphous nature. Based on the result obtained, it demonstrated that the density and molar volume increase with glass modifier content, which more attributed to the replacement of Bi_2O_3 and PbO ; both had larger density and molar volume than B_2O_3 and P_2O_5 in glass networks. The observed higher values in velocity at low modifier content and low values at high modifier content for both glass types, confirmed a substantial change in glass structure. Additional increment of Bi_2O_3 and PbO , causing more discontinuity and, hence, decrease in rigidity and velocity results.

For the thermal properties of glass, we found an interesting feature on values for glass transition temperature (T_g) in this study, where trends for borate system were inverted as compared to phosphate system. In lead bismuth borate glasses, the T_g of every glass series was decreased with increasing content of PbO and Bi₂O₃, which probably due to slightly change in the glass structure. An addition of Bi₂O₃, classified as alkaline metal oxides into the system, the bond between each atom in the sample, become weaker with increasing number of NBOs atoms. It is widely known that the bond between alkaline atom and oxygen is an ionic bond which is in general weaker than the covalent bond, thus, the bond is easier to break and hence decreases the T_g of sample.

ACKNOWLEDGEMENT

The financial support of the Ministry of Science, Technology and Innovation, Malaysia under IRPA vote 54061 is gratefully acknowledged.

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