Preparation of ternary $(35 - x)\text{Sb}_2\text{O}_3\text{-}x\text{Bi}_2\text{O}_3\text{-}65\text{P}_2\text{O}_5$ glasses for lead-free glass application

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Glasses composed of ternary components $(35 - x)\text{Sb}_2\text{O}_3\text{-}x\text{Bi}_2\text{O}_3\text{-}65\text{P}_2\text{O}_5$ ($0 \leq x \leq 20$ mol%) have been prepared and investigated as a potential alternative to lead-free glass for low temperature applications. Their structural properties were studied by Infrared Spectroscopy IR and Differential Thermal Analysis DTA. Results from the IR showed that Sb^{3+} and Bi^{3+} were responsible for glass network structure, which was supported by the diversification of density ρ and molar volume V_m with an increasing amount of Bi_2O_3 . Glass transition temperature T_g , thermal stability, and coefficient of thermal expansion increased after substitution of Bi_2O_3 for Sb_2O_3 within the range of 0 mol% to 20 mol%. The water durability decreased and then increased; it could be attributed to the corrosion resistant P–O–Sb bonds. A typical sample of $25\text{Sb}_2\text{O}_3\text{-}10\text{Bi}_2\text{O}_3\text{-}65\text{P}_2\text{O}_5$ possesses excellent properties and can be a promising candidate for further applications.

Keywords: *structure; chemical properties; bismuth phosphates*

1. Introduction

The application of low-melting glasses has been widely expanded for sealing processes in fields such as high-energy physics, aerospace, automotive industry, electronics, and coatings, because of their low transition temperature T_g , excellent chemical stability, thermal resistivity, and strong mechanical strength, etc. [1]. Most commercial sealing operations prefer lead-based sealing frits as the primary choice for materials. However, there are some serious disadvantages, such as deleterious effects on human health and environment, seriously restricting the practical utilization of lead-based glasses [2]. Therefore, research on lead-free and low-melting point glasses with excellent properties have sparked great interest in recent years.

Phosphate glass, a representative of a glass system with a high coefficient of thermal expansion α and a low T_g , is superior to silicate and borosilicate glasses as an alternative to lead-based glass for low-melting applications [3]. However, such a system suffers from low chemical durability because of the existence of easily hydrated

phosphate chains. Fortunately, this issue can be addressed by addition of oxides of trivalent metal cations such as Al_2O_3 , Fe_2O_3 , and Bi_2O_3 [4]. Outermost electrons are weakly connected because of screening by inner electrons; therefore, highly charged glass-forming ions like P^{5+} distort Bi^{3+} -ions. These deformable and asymmetric groups favor extensive glass formation [5]. Thus, $\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses are preferred in terms of environmental protection and cost benefits. To improve chemical durability of phosphate glasses, antimony trioxide is usually chosen to modify the glass structure and decrease the T_g . The electron lone pair in the Sb^{3+} -ion makes it possible [6]. Until now, no work on the development of $\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses that contain Sb_2O_3 substitutes in place of Pb-based glasses has been reported. Herein, ternary system $(35 - x)\text{Sb}_2\text{O}_3\text{-}x\text{Bi}_2\text{O}_3\text{-}65\text{P}_2\text{O}_5$ ($0 \leq x \leq 20$ mol%) glasses were fabricated and their properties were investigated in detail.

2. Experimental

The raw materials used in the preparation of $\text{Bi}_2\text{O}_3\text{-Sb}_2\text{O}_3\text{-P}_2\text{O}_5$ (BSP, hereafter) glass were of reagent grade, like antimony trioxide (Sb_2O_3), bismuth trioxide (Bi_2O_3) and phosphate (H_3PO_4).

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Firstly, the well-mixed batch materials were melted up to 1200 °C in high-purity alumina crucibles for about 1.5 h, and then quenched in a graphite mould to form a suitable glass block. Then the obtained glasses were annealed at 400 °C for 2 h in a muffle furnace and cooled down slowly to room temperature.

The bulk glasses were machined into cylinders (Φ 10 mm $\times$ 50 mm) for CTE (coefficient of thermal expansion) measurement using a horizontal dilatometer (PCY, Xiangtan Instrument, China). Then the samples were polished into cubes with a size of 5 mm $\times$ 5 mm $\times$ 20 mm to calculate the glass density, ρ , which was determined by Archimedes method. The molar volume was calculated as $V_m = \bar{M}/\rho$, where M represents the average weight of the glass composition. The remaining glass was ground into powders (through 200 mesh sieve) for the FT-IR measurement. The infrared spectra of the glasses were recorded at room temperature using the KBr disc technique with a spectrometer (PE, model spectrum One-B). X-ray diffraction patterns of the glass samples after heating were collected using an X-ray diffractometer (Rigaku D/Max-3B) with $\text{CuK}\alpha$ radiation.

The above mentioned rectangular samples (5 mm $\times$ 5 mm $\times$ 20 mm) were also used for water durability testing. The specimens were placed in a hermetically sealed glass flask with 150 mL deionized water at 90 ± 2 °C for 24 hours. The chemical durability was evaluated by calculating the weight loss of the unit area ($\text{mg}\cdot\text{cm}^{-2}$).

3. Results and discussion

3.1. Glass forming region

As illustrated in Fig. 1, the glass-forming region of the BSP system was studied in numerous experiments. Open and closed circles represent transparent and crystallized glasses respectively, while half-open circles denote opaque samples without crystallization [7]. The minimum amount of P_2O_5 required to obtain transparent glasses in the ternary system was assumed to be at 60 mol%. Moreover, the maximum amount needed to form glass in a binary Bi_2O_3 – P_2O_5 system

was calculated as 30 mol% Bi_2O_3 . The value is lower than the previously reported by Tiwari et al. [8] value of 35 mol% Bi_2O_3 . In addition, melting temperature increased from 1100 °C ($\text{Bi}_2\text{O}_3 \leq 20$ mol%) to 1200 °C ($\text{Bi}_2\text{O}_3 > 20$ mol%) at a higher amount of Bi_2O_3 . The lower glass-forming range in this system may result in the formation of BiPO_4 compound [9]. It can be concluded that Bi_2O_3 participated as a modifier in the network of these phosphate glasses. Antimony trioxide was added to decrease the T_g and increase the chemical stability of the glasses. However, the samples with a high Sb_2O_3 content (≥ 40 mol%) became opaque.

Fig. 1. Glass-forming region of BSP system.

Consequently, the maximum Sb_2O_3 content should be lower than 40 mol%. After several weeks of air exposure, the sample surfaces with $\text{P}_2\text{O}_5 \geq 70$ mol% became white because of reactions under existing humidity conditions. It is concluded that the glasses with high P_2O_5 content are not suitable for practical applications. Therefore, as indicated by the dash line in Fig. 1, the amount of P_2O_5 in this ternary system was selected at 65 mol% (Table 1).

3.2. Structure analysis

Infrared spectra of the BSP glasses are shown in Fig. 2. The results of tested samples revealed characteristic structural information. The stretching vibration band of $\text{P}=\text{O}$ bond (usually at 1240 cm^{-1} to 1270 cm^{-1} and 1320 cm^{-1}) is not observed, which implies that the $\text{P}=\text{O}$ double bond is absent in the glass samples. The symmetric vibrations

Table 1. Batch composition of the glasses in $(35 - x)\text{Sb}_2\text{O}_3 - x\text{Bi}_2\text{O}_3 - 65\text{P}_2\text{O}_5$ system [mol%].

Sample	$\text{Bi}_2\text{O}_3(x)$	$\text{Sb}_2\text{O}_5(35 - x)$	$\text{P}_2\text{O}_5(65)$
A ₁	0	35	65
A ₂	5	30	65
A ₃	10	25	65
A ₄	15	20	65
A ₅	20	15	65

of O–P–O bond of Q^2 (Q^n represents the PO_4 tetrahedron having n bridging oxygens) tetrahedron with non-bridging oxygens are observed around 1068 cm^{-1} and become boarder with increasing concentration of Bi_2O_3 [10]. The absorption peak at 736 cm^{-1} can be attributed to symmetric vibrations of P–O–P bonds in phosphate chains [11]. Therefore, it could be concluded that P_2O_5 found in the glass exists in the form of a $[\text{PO}_4]$ tetrahedron. The sharp absorption peak around 638 cm^{-1} can be assigned to the stretching vibration of P–O–Sb linkages, which indicates antimony participation in the formation of the glass network [9, 12]. The strong absorption peak at 588 cm^{-1} can be identified as bending vibrations of O–P–O bonds [13]. The main band around 505 cm^{-1} is the absorption peak of bending vibrations corresponding to P–O bonds of a Q^0 tetrahedron with several non-bridging oxygens [14]. The absorption peak at 463 cm^{-1} corresponds to the asymmetric stretching vibration of Sb–O bonds [5]. There are significant differences in the shapes of lines in the FT-IR spectra with increasing bismuth content, especially for A₄ and A₅. The P–O–Sb bonds and the Sb–O asymmetric stretching vibration become weaker with decreasing content of Sb_2O_3 . On the contrary, the absorption peak of P–O–Bi bonds is detected around 530 cm^{-1} (A₄ and A₅ in Fig. 2) [15]. The identical infrared spectrum indicates that Bi_2O_3 participates in the glass network formation creating diversity in the glass structures.

3.3. Thermal behavior

The differential thermal analysis DTA curves of the glasses are illustrated in Fig. 3. The thermal stability is confirmed by an approximate method by measuring the difference between T_x and T_g

Fig. 2. Infrared spectra of the $(35 - x)\text{Sb}_2\text{O}_3 - x\text{Bi}_2\text{O}_3 - 65\text{P}_2\text{O}_5$ glasses.

(where T_x is crystallization temperature and T_g is the glass transition temperature) using the formula $\Delta T = T_x - T_g$. The values are summarized in Table 2, where the softening temperature T_f and coefficients of thermal expansion are also included. It is seen that the tendency of variation of the T_g and T_f is consistent and the values are all higher with increasing of bismuth content compared to sample A₁ (with no Bi_2O_3). The value of ΔT increases gradually from 96°C for sample A₁ to 123°C for sample A₃ and then decreases with the further increasing of bismuth content, which indicates that sample A₃ has better thermal stability. For the samples A₂, A₃ and A₄, bismuth provides free O^{2-} anions to prompt the formation of $[\text{SbPO}_4]$ tetrahedron, which has also been confirmed by the detection of stretching vibration of P–O–Sb linkages in Fig. 2. The participation of antimony in the network can strengthen the structure of glass and correspondingly increase the vital temperatures, such

as T_g , T_f and T_x . However, with increasing Bi_2O_3 content (sample A_5), the bridging oxygen bond has been destroyed by too large number of free O^{2-} anions from A_5 and, as a result, the temperatures T_g and T_f decreased. The CTE values of the tested samples firstly decrease and get a minimum value of $9.406 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$ for sample A_3 , then increase with increasing bismuth content as shown in Table 2. It can be concluded that bismuth replaces a part of antimony as an external network. The network structure of phosphate unit is changed, which makes the rack-mounted configuration of phosphate destructive. The samples show good performance when bismuth content reaches 15 mol% in accordance with the above analysis.

Fig. 3. DTA curves of the $(35 - x)\text{Sb}_2\text{O}_3$ - $x\text{Bi}_2\text{O}_3$ - $65\text{P}_2\text{O}_5$ glasses.

3.4. Density and molar volume

The density ρ and molar volume V_m of the glasses are shown in Fig. 4. It can be concluded that ρ increases linearly from $3.51 \text{ g}\cdot\text{cm}^{-3}$ to $4.37 \text{ g}\cdot\text{cm}^{-3}$ with the increasing of Bi_2O_3 content. Evidently, the increase results mainly from the higher mass molar weight of Bi_2O_3 than that of Sb_2O_3 . Conversely, there is a linear decrease in V_m (from $55.35 \text{ cm}^3/\text{mol}$ for sample A_1 to $52.42 \text{ cm}^3/\text{mol}$ for sample A_5) of BSP in the same region.

Fig. 4. Density ρ and molar volume V_m of $(35 - x)\text{Sb}_2\text{O}_3$ - $x\text{Bi}_2\text{O}_3$ - $65\text{P}_2\text{O}_5$ glasses.

3.5. Water durability

The chemical durability of BSP glasses has been evaluated by water durability. The curves of weight loss are shown in Fig. 5. With addition of Bi_2O_3 , the values firstly decrease from $18.45 \text{ mg}\cdot\text{cm}^{-2}$ (for sample A_1) to $7.89 \text{ mg}\cdot\text{cm}^{-2}$ (for sample A_3) and then increase to $17.49 \text{ mg}\cdot\text{cm}^{-2}$ for sample A_5 . The reasons are summarized as follows:

1. Poor water durability may be associated with the rupturing of phosphate chains in the glasses and their further dissolution in water [16]. According to the literature [17], samples are corrosion resistant because of the high polarizing power of P-O-Sb bonds [18]. The FT-IR spectra indicate an increase in intensity of P-O-Sb linkages while Bi^{3+} blocks H^+ diffusion, and weakens glasses corrosion, as the network is switched from A_1 to A_3 .
2. After introduction of excess amount of Bi_2O_3 (A_4 and A_5) into the system, the stronger P-O-Sb bonds are entirely replaced by P-O-Bi bonds which exhibit lower water durability. Due to the elimination of O-P-O bonds, Sb-O bonds equally affect water durability in A_4 and A_5 networks.
3. The three-dimensional network of glasses is inferior to the $[\text{SbPO}_4]$ network. This is attributed to a higher field intensity created by Sb^{3+} ions in comparison to Bi^{3+} ones [19]. The high field intensity of P^{5+} -ions fractures Sb-O bonds and inhibits the formation of Bi-O bonds [20]. These changes cause that water durability is reduced after the first increase.

Table 2. Temperature of initial crystallization T_x , T_f , $T_x - T_g$ and α of the synthesized glasses.

Sample	T_g [± 1 °C]	T_f [± 1 °C]	T_x [± 1 °C]	α_{20-300} °C [$10^{-7}/^{\circ}\text{C}$]	$\Delta T = T_x - T_g$ [± 2 °C]
A ₁	376	411	487	11.560	111
A ₂	389	436	503	10.183	114
A ₃	400	435	528	9.406	128
A ₄	407	453	525	10.343	118
A ₅	392	441	506	11.077	114

Fig. 5. Weight loss of the glass samples from A₁ to A₅ after immersion in deionized water at 90 °C for 24 h (the error is estimated as ± 5 %).

In this study, we investigated the structure, thermal and chemical properties of ternary $(35 - x)\text{Sb}_2\text{O}_3 - x\text{Bi}_2\text{O}_3 - 65\text{P}_2\text{O}_5$ ($0 \leq x \leq 20$) glasses. The substitution of Sb_2O_3 with Bi_2O_3 transformed the network structure, decreased its thermal stability and altered the water durability. In addition, Sb_2O_3 dominated water durability in the x range from 0 to 10, as the glass network was connected with $[\text{PO}_4]$ tetrahedral. The variations in chemical and thermal properties of the glass system can be attributed to the change in glass structure. FT-TR analysis revealed that the excess of Bi_2O_3 ($x = 15$ to 20) could damage P–O–Sb bonds, O–P–O bonds and Sb–O bonds to produce P–O–Bi bonds, which made the water durability poor. The DTA results illustrate that Bi_2O_3 may influence the thermal stability and glass forming ability through providing free O^{2-} anions altering the network structure.

Acknowledgements

Grateful acknowledgement is made to the support from the National Natural Science Foundation of China (61275057). The work was also financed by the Ministry of Education, Liaoning Province of China, under Project L2014226.

References

- [1] GU S.Y., WANG Z.Q., JIANG S.W., LIN H., *Ceram. Int.*, 40 (2014), 7643.
- [2] HUANG B., GAN W.P., GUO G.G., LI Y., LIU X., *Ceram. Int.*, 40 (2014), 393.
- [3] BOBKOV A.N.M., *J. Glass. Phys. Chem. Glasses*, 38 (2012), 180.
- [4] MASSERA J., BOURHIS K., PETIT L., COUZI M., HUPA L., HUPA M., VIDEAU J. J., CARDINAL T.J., *J. Phys. Chem. Solids*, 74 (2013), 121.
- [5] LI H. Y., ZHU Z.L., YANG F.L., *J. Int. J. Min. Met. Mater.*, 19 (2012), 628.
- [6] KIM H.J., JE S.Y., JU Y.W., BAEK J.H., JEONG J.K., *Phys. Status Solidi R*, 8 (2014), 924.
- [7] CICEO R.L., TRANDAFIR D.L., RADU T., PONTA O., SIMON V., *Ceram. Int.*, 40 (2014), 9517.
- [8] TIWARI A.N., SUBBARAO E.C., *J. Am. Ceram. Soc.*, 53 (1970), 258.
- [9] ZHANG B., CHEN Q., SONG L., LI H., HOU F., *J. Am. Ceram. Soc.*, 91 (2008), 2036.
- [10] QI Y.J., WANG Z.Q., ZHAI S.R., *Mater. Sci. -Poland*, 32 (2014), 414.
- [11] EFIMOV A.M., *J. Non-Cryst. Solids*, 209 (1997), 213.
- [12] ZHANG B., CHEN Q., SONG L., *J. Non-Cryst. Solids*, 354 (2008), 1948.
- [13] HAFID M., JERMOUMI T., TOREIS N., GHAILASSI T., *Mater. Lett.*, 56 (2002), 486.
- [14] TANG G., LI J., LU A.X., *J. Mater. Rev.*, 1 (2012), 122.
- [15] CHAHINE A., ET-TABIROU M., PASCAL J.L., *J. Mater. Lett.*, 58 (2004), 2776.
- [16] MENAA B., MIZUNO M., TAKAHASHI M., TOKUDA Y., YOKO T., *J. Solid State Chem.*, 179 (2006), 492.
- [17] GOLOVIN A.I., PAVLOVSKI V.K., SHCHAVELEV O.S., *Glass. Ceram.*, 49 (1993), 513.
- [18] ZHANG B., CHEN Q., SONG L., LI H., ZHANG J., *J. Non-Cryst. Solids*, 354 (2008), 1948.

- [19] LI H.Y., ZHU Z.L., YANG F.L., ZHANG W.D., *Vac. Sci.*, 3 (2012), 43.
- [20] WANG M.Q., XIONG G.H., ZHANG R.C., *J. China Ceram. Soc.*, 20 (1992), 457.

Received 2017-05-04

Accepted 2018-10-24