FULL PAPER

Effect of Bi_2O_3 on thermal, chemical durability, and bonding properties of $\text{V}_2\text{O}_5\text{--P}_2\text{O}_5\text{--TeO}_2$ glasses for low-temperature sealing glassJae-Young SHIN¹, Jaemin CHA² and Bong-Ki RYU^{1,†}¹Division of Materials Science and Engineering, Pusan National University, B05-2410 Jangjeon-dong, Geumjeong-gu, Busan, Korea²The Institute of Materials Technology, Pusan National University, B05-2410 Jangjeon-dong, Geumjeong-gu, Busan, Korea

Lead-free low-melting sealing materials are needed in many fields, especially in organic light-emitting diode and Vacuum-Insulated Glass applications. Accordingly, $\text{V}_2\text{O}_5\text{--P}_2\text{O}_5\text{--TeO}_2$ (VPTe) glass systems have been invested in as lead-free low-melting sealing materials because of their low coefficient of thermal expansions (CTE) and glass transition temperature (T_g). However, these glasses are vulnerable to moisture. This problem can be overcome by adding bismuth oxide to the VPTE glass system. The addition of 9 mol % of Bi_2O_3 improves water resistance, and causes changes in the T_g increased about 40°C and the CTE decreased about 14 ($\times 10^{-7}/\text{K}$) that may reflect the structural changes. As a result, the glasses, which are doped with Bi_2O_3 , maintain their low-temperature properties, and they are improved their water resistance about $1.2 \times 10^{-5} (\text{g}/\text{cm}^2/\text{min})$.

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1. Introduction

Lead-free low-melting sealing materials are necessary in many fields, especially in organic light-emitting diode (OLED) and Vacuum-Insulated Glass (VIG) applications.¹⁾ Especially, heat-tempered glass substrates used in the VIG application lose functionality above a certain temperature ($<400^\circ\text{C}$). Therefore, there is a restriction on the sealing temperature. Accordingly, $\text{V}_2\text{O}_5\text{--P}_2\text{O}_5\text{--TeO}_2$ (VPTE) glass systems have been invested in as lead-free low-melting sealing materials because of their low coefficient of thermal expansions (CTE) and glass transition temperature (T_g). However, these glasses are vulnerable to moisture.^{2),3)} This vulnerability to water resistance is a common phenomenon in phosphate-contained glasses.^{4),5)} This study overcomes this problem by adding Bi_2O_3 to the VPTE glass, which enhances water resistance. The bonding strength is also required in sealing materials.^{1),6)} Bonding properties are one of the important properties that need to be evaluated in the everyday use of sealing glass. The bonding phenomenon occurs through the 1st wetting and 2nd bonding operation, and the effects of both the 1st and 2nd steps affect the bonding strength.⁷⁾ Wetting of glass sealant is related to thermal properties such as T_g . Thus, a glass with a lower T_g is able to be used at lower temperatures. Therefore, this study investigates the effect of adding Bi_2O_3 to the VPTE glass system on the water resistance properties, how thermal properties (e.g., T_g)

change, and how it affects the bonding strength.

2. Experimental procedure

2.1 Glass preparation

Glass samples with a composition of $60\text{V}_2\text{O}_5\text{--}25\text{P}_2\text{O}_5\text{--}15\text{TeO}_2$ adding $x\text{Bi}_2\text{O}_3$ ($x = 0, 3, 6$ and 9 mol %) were prepared using V_2O_5 , P_2O_5 , TeO_2 , and Bi_2O_3 obtained from the Junsei Chemical Co. (Japan). To select basic composition, we examined $\text{V}_2\text{O}_5\text{--P}_2\text{O}_5\text{--TeO}_2$ glass system containing 60 mol % V_2O_5 . The increase in P_2O_5 content from 5 to 35 mol % lowered the CTE and made samples be too vulnerable to moisture. When considering water resistance and the CTE with the soda lime glass substrate (CTE about $80\text{--}90 \times 10^{-7}/\text{K}$), we concluded the composition of $60\text{V}_2\text{O}_5\text{--}25\text{P}_2\text{O}_5\text{--}15\text{TeO}_2$ is suitable for basic composition and proceeded this experiment. In this research, the amount of Bi_2O_3 contents were restricted under 9 mol % because samples which were added over the 9 mol % of Bi_2O_3 could not be sintered at 400°C . Each sample batch was mixed and repeatedly ground for homogenization. The batches were melted at 950°C in an alumina crucible under normal atmospheric conditions for no more than 60 min to minimize the volatilization of the glass components.

2.2 Measurements

The amorphous state of the samples was confirmed by X-ray diffractometry (XRD, Rigaku-Ultima IV). The thermal properties of the glasses were measured using a thermo-mechanical analyzer (TMA) at a heating rate of $10^\circ\text{C}/\text{min}$. The TMA curves yielded the T_g and the deformation temperature (T_d). The chemical durability was

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evaluated from their dissolution rates (*DR*) in distilled water at 90°C. Cylindrical pellets were made by compressing the powder (3 g, $\leq 45\ \mu\text{m}$) and placing in distilled water for 48 h. The weight loss was then measured using an electronic scale. The *DR* was calculated from the expression $DR = \Delta w/S$, where Δw is the weight loss (g), and *S* is the sample area (cm²) before the dissolution test. The structure of the glass samples was analyzed by Fourier transform infrared (FT-IR) spectroscopy (KBr, Spectrum GX, 400–1400 cm⁻¹). X-ray photoelectron spectroscopy (XPS) measurements were also performed to observe the change in the valence of Vanadium caused by the Bi₂O₃ addition. The bonding strength test was performed by placing a pellet on a soda lime glass substrate, subjecting the glass plate to primary firing at 350°C for 30 min, then place the top soda lime glass plate and subjecting the specimen to secondary firing at 400°C for 30 min. The bonding strength was measured with a universal testing machine (RB 302ML, Korea), and the average value was measured five times at a speed of 6.0 mm/min. The interface between the soda-lime glass substrate and the glass powder to be observed was measured using a transmission electron microscope (TALOS F200X) using an applied voltage of 200 kV. The ionic diffusion behavior between substrate and sealing layer affecting bonding property was confirmed by electron dispersive X-ray (EDX) analysis.

3. Results and discussion

3.1 Composition range of the glass formation

Figure 1 shows the XRD data for the 60V₂O₅-25P₂O₅-15TeO₂ adding Bi₂O₃ (where *x* = 0, 3, 6 and 9 mol %) samples. The experimental compositions formed the glass well. The XRD data indicate a conventional amorphous phase.

3.2 Structural properties

Phosphate-added glasses have low water resistance, while weak P–O–P bonds are easily hydrated.^(4,5) There have been many studies to increase the water resistance by adding the other additive elements.^(8,9) **Figure 2** shows

Fig. 1. XRD patterns of the 60V₂O₅-25P₂O₅-15TeO₂ adding *x*Bi₂O₃ (where *x* = 0, 3, 6 and 9 mol %).

FT-IR spectra of the glasses over the range 400–1400 cm⁻¹. The relative intensity of the band for the P–O⁻ units to that of other structural units is decreased with an increase in Bi₂O₃ content at 1080 cm⁻¹. As Bi₂O₃ contents added, there is decrease in the relative intensity of the PO₂ symmetric stretching band to that of other structural units and this band shifts towards a lower frequency (from 1243 to 1237 cm⁻¹) and there is decrease in the relative intensity of the PO₂ asymmetric stretching band to that of other structural units and this band shifts towards a lower frequency (from 1280 to 1270 cm⁻¹). The peak near 1000 cm⁻¹ means (PO₃)_s of the phosphate Q¹ structure, and there is increase in the relative intensity to that of other structural units and shift towards higher frequency (1010 cm⁻¹) as the amount of Bi₂O₃ increases. This phenomenon indicates that the Q²(PO₂) long-chain structures change to Q¹(PO₃) short-chain structures. The stretching vibration of PO₃ groups is an indication of the increasing covalent character of the Bi–O–P bond. This covalent character is in favor of the glass forming ability of Bi³⁺ ions. Several authors reported that in the glasses containing bismuth oxide, the glass forming nature of Bi³⁺ can be confirmed by presence of highly distorted BiO₆ polyhedra.^(10,11) It can be explained by the peak in the range of 450–550 cm⁻¹.

For no addition of Bi₂O₃, the band that appears in the region 450–550 cm⁻¹ is caused by the deformation vibration of the phosphate groups.^(10,12) However, upon addition of Bi₂O₃, the Bi–O bonds are formed from the distortion of BiO₆ octahedra, and the deformation vibrations of the phosphate groups appear in the overlapping vibrations.^(13,14) Also, upon Bi₂O₃ addition, the phosphate group deformation shift towards a higher frequency. This phenomenon observed within the region 450–550 cm⁻¹ is related to the vibration of the Bi–O bonds.^(11,12) The relative intensity of 880 cm⁻¹, which means the asymmetric stretching of P–O–P group, decreases with increasing Bi₂O₃ content. This indicates that phosphate chains are depolarized by the incorporation of Bi³⁺ via P–O–Bi bonds, with an increase in the (PO₃)_s group.⁽¹²⁾ The bismuth-oxygen bond is more covalent than the phos-

Fig. 2. FT-IR spectra of 60V₂O₅-25P₂O₅-15TeO₂ adding *x*Bi₂O₃ (where *x* = 0, 3, 6 and 9 mol %).

phate-oxygen bond, and the phosphorus-oxygen bonds linked to bismuth ions P–O(Bi) are more ionic than P–O–P bonds. This means that the structure of the Bi₂O₃ doped-glass is denser than the reference glass.¹²⁾

3.3 Thermo-mechanical properties

Figure 3 and **Table 1** show the thermal analyses of 60V₂O₅–25P₂O₅–15TeO₂ adding *x*Bi₂O₃ (where *x* = 0, 3, 6 and 9 mol %). The *T_g* and the *T_d* increase with the increasing Bi₂O₃ content.

The CTE slightly increase when the Bi₂O₃ is added for the first time, but decrease as the amount of Bi₂O₃ increased. The tendency of increasing *T_g* and decreasing CTE tend to occur when the glass networks are densified.¹⁵⁾ Therefore, effect of the Bi₂O₃ addition is confirmed to change from Q²(PO₂) to Q¹(PO₃), then the glass structure is densified. The CTE is reduced to 80 (×10^{−7}/K) or less when Bi₂O₃ up to 9 mol % is added. Furthermore, *T_g* is less than 350°C; hence, it could be applied as a low expansion glass. These properties are likely to be seen in a low-temperature sealing glass.

3.4 Chemical durability

There were some reports about relationship between the dissolution rate and glass structure. They explained The dissolution rate of glass increases when the glass structure is weakened.^{16),17)} **Figure 4** presents weight loss as a function of time for the glass samples with different Bi₂O₃ levels. The VPTe sample has the highest weight loss (5.2·10^{−2} g·cm^{−2}) at 48 h, while the VPTe–Bi3 (3.2·10^{−2} g·cm^{−2}) and VPTe–Bi6 (3.5·10^{−2} g·cm^{−2}) samples have smaller weight losses, which are similar to each other. the VPTe–Bi9 (1.6·10^{−2} g·cm^{−2}) with the largest Bi₂O₃ con-

Fig. 3. Thermal properties of 60V₂O₅–25P₂O₅–15TeO₂ adding *x*Bi₂O₃ (where *x* = 0, 3, 6 and 9 mol %).

tent has smaller weight loss values. The slope (weight loss against time) for VPTe is higher than those for the other samples. The DR results indicate chemical durability. The non Bi₂O₃-doped sample (VPTe) had a higher slope than those doped with Bi₂O₃. This result shows that VPTe is easily dissolved in water, and has the least chemical durability. In contrast, the samples doped with the Bi₂O₃ contents have a lower slope and a tendency toward a higher chemical durability with increased doping levels. This result can be proven by the IR and TMA results. The tendency to decrease the *T_g* and increase the CTE is densifying and indicates the change of the glass structure. As Bi₂O₃ is added, the Q²(PO₂) long-chain structures change to Q¹(PO₃) short-chain structures. And The weak P–O–P bonds, which are easily hydrated, are replaced to the P–O–Bi bonds. This effect can promote chemical durability (i.e., against water corrosion). The improvement in the chemical durability can further enhance its applicability as a low-temperature sealing glass.

3.5 Bonding property

Figure 5 represents the average value of the bonding strength when the amount of added Bi₂O₃ is increased. The bonding strength of VPTe–Bi3 added with 9 mol % Bi₂O₃ is the highest at 10.1 MPa. The glass without Bi₂O₃ is measured to the lowest strength at 8.9 MPa. The evaluation of bonding property shows that the bonding strength has the tendency to increase as the amount of Bi₂O₃ increased.

Such a change in the bonding strength is depended on the reaction between the sealing glass and the glass sub-

Fig. 4. Weight loss of the 60V₂O₅–25P₂O₅–15TeO₂ adding *x*Bi₂O₃ (where *x* = 0, 3, 6 and 9 mol %) glasses at 90°C in distilled water for 48 h.

Table 1. Composition and properties of the VPTe glass system

Samples	Composition (mol %)				<i>T_g</i> (°C)	<i>T_d</i> (°C)	CTE (10 ^{−7} /K)	Samples that immersed for 48 h		Bonding strength (MPa)
	V ₂ O ₅	P ₂ O ₅	TeO ₂	Bi ₂ O ₃				DR (g/cm ² /min)	pH	
VPTe	60	25	15	—	265.10	280.35	85.00	1.8 × 10 ^{−5}	7.05	8.9
VPTe–Bi3	60	25	15	3	291.25	312.28	88.79	1.11 × 10 ^{−5}	7.14	9.5
VPTe–Bi6	60	25	15	6	298.08	328.76	80.84	1.22 × 10 ^{−5}	7.18	9.7
VPTe–Bi9	60	25	15	9	312.64	341.02	71.76	0.56 × 10 ^{−5}	7.33	10.1

strate. Therefore, the addition of Bi_2O_3 affects the reaction between the sealing glass and the glass substrate.

3.6 Interface between the sealing glass and the substrate

Figure 6 indicates the TEM measurement of the cross-section of the specimen with the soda lime substrate adhered at 400°C with the composition without Bi_2O_3 and with 9 mol % of Bi_2O_3 addition as the sealing glass. The contrast difference in the TEM image is indicated by the

Fig. 5. Bonding strength of $60\text{V}_2\text{O}_5$ - $25\text{P}_2\text{O}_5$ - 15TeO_2 adding $x\text{Bi}_2\text{O}_3$ (where $x = 0, 3, 6$ and 9 mol %).

constituent elements. The Si is composition from soda lime glass used as substrate, and V, P and Te are compositions from sealing glass. The sealing glass is composed of elements heavier than those in the soda lime glass. Therefore, the sealing glass seems darker than soda lime glass in TEM image. The dark part in the image is the sealing glass, whereas the bright part is the soda lime glass. A layer with intermediate contrast was formed at the interface between the sealing glass and the soda lime glass. The intermediate contrast layer can be higher molecular weight than the soda lime glass, where the average molecular weight of the constituent elements was lower than that of the sealing glass. The width of the intermediate layer was approximately 16 nm in the case of VPTe without Bi_2O_3 and approximately 20 nm in the case with 9 mol % Bi_2O_3 added.

Figure 7 shows the data obtained by EDX line scanning to analyze the composition of the intermediate layer on the TEM image. The diffusion reaction occurred at the interface despite of the Bi_2O_3 addition. The diffusion distance is similar to the width of the intermediate layer in Fig. 6. Therefore, the intermediate layer on the TEM image is confirmed that element diffused and existed.

The addition of Bi_2O_3 increases the width of the intermediate layer (i.e., the diffusion distance is increased). The diffusion is known to increase the adhesive strength through the diffusion theory of the adhesion mechanism.^{18),19)} As a result, the bonding strength caused by the

Fig. 6. TEM image of the interface between the substrate and the sealing glass at different Bi_2O_3 contents

Fig. 7. Element distribution in the cross-sections of the specimen observed by EDX analysis.

Bi₂O₃ addition is increased because of the increase of the diffusion distance.

3.7 V 2p spectra

Vanadium oxide is variously present as VO, VO₂, V₂O₃, and V₂O₅.^{20),21)} The reduction of V⁵⁺ to V⁴⁺ is formed by the reduction reaction of V₂O₅ to VO₂ [Eq. (1)] and seems to be structurally changed as in Eq. (2) as the Bi₂O₃ content increases.

The ratio of V⁴⁺ to V⁵⁺ in the vanadium glass according to addition of Bi₂O₃ is confirmed. The correlation between the structural changes of the glass sintered body and the changes of PO₄ and PO₃ can be confirmed in Fig. 2, which is the result of the FT-IR. An XPS analysis is performed to confirm the content of V⁵⁺ and V⁴⁺ with the Bi₂O₃ addition (Fig. 8). The V₂P_{3/2} peak at each composition was separated by V⁵⁺ (near 517 eV) and V⁴⁺ (near 516 eV) using the Gaussian peak separation method.²¹⁾ Table 2 shows the quantitative quantities of V⁵⁺/V_{total} and V⁴⁺/V_{total}. The increase in content of V⁴⁺ with the Bi₂O₃ addition meant a reduction reaction from V⁵⁺ to V⁴⁺ occurred. The proportion of the VO₄ polyhedron is expected to increase compared to that of the VO₅ polyhedron. These changes affect the diffusion behavior of the Si species in

Fig. 8. High-resolution V 2p spectra for the 60V₂O₅-25P₂O₅-15TeO₂ adding *x*Bi₂O₃ (where *x* = 0, 3, 6 and 9 mol %).

Table 2. Fit parameters for the V 2P_{3/2} variation of V⁵⁺ and V⁴⁺ with the Bi₂O₃ content

Samples	Peak BE	Area	V ⁵⁺ Ratio (%)	V ⁴⁺ Ratio (%)
VPTe	515.76	282	96.07	3.93
	517.33	6892		
VPTe-Bi3	515.71	438	94.03	5.97
	517.11	6896		
VPTe-Bi6	516.10	487	91.09	6.91
	517.47	6562		
VPTe-Bi9	516.15	628	91.35	8.65
	517.45	6636		

Fig. 7. the addition of Bi₂O₃ in the V₂O₅ glass structure, in which V⁴⁺ and V⁵⁺ coexisted but V⁴⁺ ratio increased from 3.93 to 8.65%.

In other words, The skeleton of the network structure changes from two-dimensional layer structure composed of VO₅ tetragonal pyramids, to three-dimensional network structure composed of VO₄ tetrahedra.²²⁾ It is worth noting this phenomenon causes a long-range structural change from the original two-dimensional layer structure to a one-dimensional chain structure composed of VO₄ tetrahedra. Therefore, this change results in a depolymerization of the glass matrix and being a less complicated glass matrix. It is able to increase mobility of ions due to an increased space or tunnel within the matrix.²²⁾ These changes in skeleton of the network structure is considered to be an advantageous structure for further diffusion of the Si species as the ratio of V⁴⁺ increased.

4. Conclusions

A V₂O₅-P₂O₅-TeO₂ glass composition with low-temperature thermal properties was designed to develop a low-temperature sealing glass composition. The Bi₂O₃ contents are added to improve the water resistance of VPTE glass system. Consequently, the PO₂ structure changed to the PO₃ structure. And the weak P-O-P bonds, which are easily hydrated, are replaced to the P-O-Bi bonds. Then, the water resistance and *T_g* were increased. Moreover, the bonding strength was increased about 2 MPa with the Bi₂O₃ addition. It is considered that the ratio of V⁴⁺ ions in the glass system glass are increased. So It is able to increase mobility of ions. Hence, the diffusion of the Si species in the substrate was believed to be favored as the ratio of V⁴⁺ ions increased. The ion diffusion distance between the substrate and the sealing layer influences the improvement of the bonding strength.

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