Effect of Bi$_2$O$_3$ on thermal, chemical durability, and bonding properties of V$_2$O$_5$–P$_2$O$_5$–TeO$_2$ glasses for low-temperature sealing glass

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Lead-free low-melting sealing materials are needed in many fields, especially in organic light-emitting diode and Vacuum-Insulated Glass applications. Accordingly, V$_2$O$_5$–P$_2$O$_5$–TeO$_2$ (VPTe) glass systems have been investigated 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$_2$O$_3$ improves water resistance, and causes changes in the $T_g$ increased about 40°C and the CTE decreased about 14 ($\times10^{-5}$/K) that may reflect the structural changes. As a result, the glasses, which are doped with Bi$_2$O$_3$, maintain their low-temperature properties, and they are improved their water resistance about 1.2 $\times 10^{-5}$ (g/cm$^2$/min).

Key-words : Lead-free low-melting sealing glass, Thermal property, Water resistance, Bonding strength

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°C). Therefore, there is a restriction on the sealing temperature. Accordingly, V$_2$O$_5$–P$_2$O$_5$–TeO$_2$ (VPTe) glass systems have been investigated 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$_2$O$_3$ 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$_2$O$_3$ 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 60V$_2$O$_5$–25P$_2$O$_5$–15TeO$_2$ adding $x$Bi$_2$O$_3$ ($x = 0, 3, 6$ and $9$ mol %) were prepared using V$_2$O$_5$, P$_2$O$_5$, TeO$_2$, and Bi$_2$O$_3$ obtained from the Junsei Chemical Co. (Japan). To select basic composition, we examined V$_2$O$_5$–P$_2$O$_5$–TeO$_2$ glass system containing 60 mol % V$_2$O$_5$. The increase in P$_2$O$_5$ 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 80–90 $\times 10^{-7}$/K), we concluded the composition of 60V$_2$O$_5$–25P$_2$O$_5$–15TeO$_2$ is suitable for basic composition and proceeded this experiment. In this research, the amount of Bi$_2$O$_3$ contents were districted under 9 mol % because samples which were added over the 9 mol % of Bi$_2$O$_3$ 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°C/min. The TMA curves yielded the $T_g$ and the deformation temperature ($T_d$). The chemical durability was
evaluated from their dissolution rates (DR) in distilled water at 90°C. Cylindrical pellets were made by compressing the powder (3 g, ≤45 μm) 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 \( \Delta w \) is the weight loss (g), and \( S \) is the sample area (cm\(^2\)) 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 Bi\(_2\)O\(_3\) addition. The bonding strength test was performed by placing a pellet on a soda lime glass substrate, subjecting the glass plate to primary ring at 400°C for 30 min, and 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 60V\(_2\)O\(_5\)–25P\(_2\)O\(_5\)–15TeO\(_2\) adding Bi\(_2\)O\(_3\) (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 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 Bi\(_2\)O\(_3\) content at 1080 cm\(^{-1}\). As Bi\(_2\)O\(_3\) contents added, there is decrease in the relative intensity of the PO\(_2\) 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 PO\(_2\) 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 (PO\(_3\))\(_3\) of the phosphate Q\(^1\) 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 Bi\(_2\)O\(_3\) increases. This phenomenon indicates that the Q\(^0\)(PO\(_3\)) long-chain structures change to Q\(^1\)(PO\(_3\)) short-chain structures. The stretching vibration of PO\(_3\) 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 Bi\(^{3+}\) ions. Several authors reported that in the glasses containing bismuth oxide, the glass forming nature of Bi\(^{3+}\) can be confirmed by presence of highly distorted BiO\(_6\) polyhedra.\(^{10,11}\) It can be explained by the peak in the range of 450–550 cm\(^{-1}\).

For no addition of Bi\(_2\)O\(_3\), 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 Bi\(_2\)O\(_3\), the Bi–O bonds are formed from the distortion of BiO\(_6\) octahedra, and the deformation vibrations of the phosphate groups appear in the overlapping vibrations.\(^{13,14}\) Also, upon Bi\(_2\)O\(_3\) 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 Bi\(_2\)O\(_3\) content. This indicates that phosphate chains are depolarized by the incorporation of Bi\(^{3+}\) via P–O–Bi bonds, with an increase in the (PO\(_3\))\(_3\) group.\(^{12}\) The bismuth-oxygen bond is more covalent than the phos-
3.3 Thermo-mechanical properties

Figure 3 and Table 1 show the thermal analyses of 60V2O5–25P2O5–15TeO2 adding xBi2O3 (where x = 0, 3, 6 and 9 mol %). The Tg and the Td 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 Tg and decreasing CTE tend to occur when the glass networks are densified.\textsuperscript{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\textsuperscript{-7}/K) or less when Bi2O3 up to 9 mol% is added. Furthermore, Tg is less than 350°C; hence, it could be applied as a low-temperature sealing 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.\textsuperscript{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\textsuperscript{-2}g·cm\textsuperscript{-2}) at 48 h, while the VPTe–Bi3 (3.2·10\textsuperscript{-2} g·cm\textsuperscript{-2}) and VPTe–Bi6 (3.5·10\textsuperscript{-2} g·cm\textsuperscript{-2}) samples have smaller weight losses, which are similar to each other. the VPTe–Bi9 (1.6·10\textsuperscript{-2}g·cm\textsuperscript{-2}) with the largest Bi2O3 content 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 Tg 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. 3. Thermal properties of 60V2O5–25P2O5–15TeO2 adding xBi2O3 (where x = 0, 3, 6 and 9 mol %).](image)

![Fig. 4. Weight loss of the 60V2O5–25P2O5–15TeO2 adding xBi2O3 (where x = 0, 3, 6 and 9 mol %) glasses at 90°C in distilled water for 48 h.](image)

| Samples | Composition (mol %) | TeO2 | Bi2O3 | Tg (°C) | Td (°C) | CTE (10\textsuperscript{-7}/K) | Samples that immersed for 48 h | Bonding strength (MPa) |
|---------|---------------------|------|-------|---------|---------|----------------|-----------------------------|----------------------|
| VPTe    | 60 25 15 —           | 60   | 25    | 265.10  | 280.35  | 85.00          | 1.8 × 10\textsuperscript{-5} | 7.05                 | 8.9                 |
| VPTe–Bi3| 60 25 15 3           | 60   | 25    | 291.25  | 312.28  | 88.79          | 1.11 × 10\textsuperscript{-5} | 7.14                 | 9.5                 |
| VPTe–Bi6| 60 25 15 6           | 60   | 25    | 298.08  | 328.76  | 80.84          | 1.22 × 10\textsuperscript{-5} | 7.18                 | 9.7                 |
| VPTe–Bi9| 60 25 15 9           | 60   | 25    | 312.64  | 341.02  | 71.76          | 0.56 × 10\textsuperscript{-5} | 7.33                 | 10.1                |
strate. Therefore, the addition of Bi$_2$O$_3$ 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$_2$O$_3$ and with 9 mol% of Bi$_2$O$_3$ addition as the sealing glass. The contrast difference in the TEM image is indicated by the 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 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$_2$O$_3$ and approximately 20 nm in the case with 9 mol% Bi$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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

![Graph](image)

**Fig. 5.** Bonding strength of 60V$_2$O$_5$–25P$_2$O$_5$–15TeO$_2$ adding $x$Bi$_2$O$_3$ (where $x = 0$, 3, 6 and 9 mol%).

![Images](image)

**Fig. 6.** TEM image of the interface between the substrate and the sealing glass at different Bi$_2$O$_3$ contents

![Images](image)

**Fig. 7.** Element distribution in the cross-sections of the specimen observed by EDX analysis.
B\textsubscript{2}O\textsubscript{3} addition is increased because of the increase of the diffusion distance.

### 3.7 V 2p spectra

Vanadium oxide is variously present as VO, VO\textsubscript{2}, V\textsubscript{2}O\textsubscript{3}, and V\textsubscript{2}O\textsubscript{5}.\textsuperscript{20,21} The reduction of V\textsuperscript{5+} to V\textsuperscript{4+} is formed by the reduction reaction of V\textsubscript{2}O\textsubscript{3} to VO\textsubscript{2} [Eq. (1)] and seems to be structurally changed as in Eq. (2) as the Bi\textsubscript{2}O\textsubscript{3} content increases.

\[ \text{V}_2\text{O}_3 \rightarrow \text{V}_3\text{O}_7 \rightarrow \text{V}_4\text{O}_9 \rightarrow \text{V}_6\text{O}_{13} \rightarrow \text{VO}_2 \]  

\[ \text{PO}_2 + V^{5+}(\text{V}_2\text{O}_3) \rightarrow \text{PO}_3 + V^{4+}(\text{VO}_2) \]  

The ratio of V\textsuperscript{4+} to V\textsuperscript{5+} in the vanadium glass according to addition of Bi\textsubscript{2}O\textsubscript{3} is confirmed. The correlation between the structural changes of the glass sintered body and the changes of PO\textsubscript{3} and PO\textsubscript{4} can be confirmed in Fig. 2, which is the result of the FT-IR. An XPS analysis is performed to confirm the content of V\textsuperscript{5+} and V\textsuperscript{4+} with the Bi\textsubscript{2}O\textsubscript{3} addition (Fig. 8). The V\textsubscript{2}P\textsubscript{3}/2 peak at each composition was separated by V\textsuperscript{5+} (near 517 eV) and V\textsuperscript{4+} (near 516 eV) using the Gaussian peak separation method.\textsuperscript{21} Table 2 shows the quantitative quantities of V\textsuperscript{5+}/V\textsubscript{total} and V\textsuperscript{4+}/V\textsubscript{total}. The increase in content of V\textsuperscript{4+} with the Bi\textsubscript{2}O\textsubscript{3} addition meant a reduction reaction from V\textsuperscript{5+} to V\textsuperscript{4+} occurred. The proportion of the VO\textsubscript{4} polyhedron is expected to increase compared to that of the VO\textsubscript{3} polyhedron. These changes affect the diffusion behavior of the Si species in 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.\textsuperscript{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 V\textsuperscript{4+} increased.

### 4. Conclusions

A V\textsubscript{2}O\textsubscript{5}–P\textsubscript{2}O\textsubscript{5}–TeO\textsubscript{2} glass composition with low-temperature thermal properties was designed to develop a low-temperature sealing glass composition. The Bi\textsubscript{2}O\textsubscript{3} contents are added to improve the water resistance of VPTe glass system. Consequently, the PO\textsubscript{3} structure changed to the PO\textsubscript{4} 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 Bi\textsubscript{2}O\textsubscript{3} addition. It is considered that the ratio of V\textsuperscript{4+} ions in the glass system is 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 V\textsuperscript{4+} ions increased. The ion diffusion distance between the substrate and the sealing layer influences the improvement of the bonding strength.

### Acknowledgement

This research was supported by the Ministry of Trade, Industry & Energy (MOTIE), Korea Institute for Advancement of Technology (KIAT) and Ulsan Institute For Regional Program Evaluation (IRPE) through the Encouragement Program for The Industries of Economic Cooperation Region.

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