Study of Water Resistance of Fe₂O₃ Doped P₂O₅–ZnO–Bi₂O₃ Sealing Glass System

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Abstract: In order to strengthen the structure of the glass and ultimately improve its water resistance, P₂O₅–ZnO–Bi₂O₃ was doped with Fe₂O₃, which generated Fe ions in the phosphate-based glass. These ions constitute (P₂O₇)⁴⁻ groups within the glass network. Structural analysis using Fourier transfer infrared spectroscopy indicated that P–O–P and Bi–O–P bonds decreased and Fe–O–P bonds increased, as a function of the Fe₂O₃ level. The thermal property analysis found that the softening point (T_s) and glass transition point (T_g) increased approximately as much as 60 and 105 °C, respectively, and the coefficient of thermal expansion decreased approximately by $25 \times 10^{-7} \text{ K}^{-1}$. The contact angle was measured to quantify the wetting property. The contact angle increased from 42.6° to 64.1° with increasing levels of Fe₂O₃ at 850 °C. As an indication of water resistance, the weight loss of the 10 mol-% Fe₂O₃-doped glass was 0.00514 g cm⁻², while that of the undoped glass was 0.00710 g cm⁻².

(Received September 16, 2015; Accepted April 5, 2016)

Keywords: glasses, sintering, corrosion, thermal analysis, water resistance.

1. INTRODUCTION

Today sealing glasses are used extensively in electronic devices such as mobile displays and solid oxide fuel cells (SOFCs) [1,2]. To meet performance requirements, they need to have proper wetting properties at their operating temperature, adequate thermal properties, and excellent water resistance [3]. Phosphate glass has a low glass transition temperature and softening point [4-6], and for these reasons, its use for sealing has been researched at length. However, phosphate glass has a lower water resistance than other glass systems because of its weak structure [7,8]. This can be a critical disadvantage for applications in certain working environments.

Until now, many studies have been conducted to lower the T_g and T_s, of glasses by adding metal oxides like PbO and Bi₂O₃ to enhance their properties as sealing glass. However, PbO is not available as an additive, because environmental regulations have prohibited its use [9]. Accordingly, Bi₂O₃ is used extensively as an alternative to PbO, because the Bi³⁺ ion is similar to Pb²⁺, for example, their atomic weights and ion radii are similar to each other [2]. In our previous study,

we confirmed through analyses of thermal and wetting properties the possibility of using P₂O₅–ZnO–Bi₂O₃ ternary glasses for sealing glass applications [2]. In that study, the Bi³⁺ ion was found to generate weak electric field intensity, so Bi₂O₃ made glass weaker by increasing the number of Bi–O bonds [2,10-12]. Therefore, it was determined that Bi³⁺ was not ideal for forming glass networks, which led to the lower water resistance of glasses modified by Bi₂O₃ [13].

Materials that can improve the water resistance of phosphate glasses are metal oxides such as Al₂O₃, Fe₂O₃, ZrO₂, MnO₂ and TiO₂ [14,15]. These materials make glass more rigid by enabling the formation of the Mn⁺–O–P bond [14,15]. Among them, Fe₂O₃ has been reported to have excellent water resistance in phosphate glasses [10]. Ordinary phosphate glasses share their corners and form tetrahedral chains and isolated PO₄ group and rings [16,17]. On the other hand, in Fe₂O₃-doped phosphate glasses, the Fe²⁺ and Fe³⁺ ions form FeO₆ groups [16]. Cross bonding of the phosphate chain is induced by the Fe³⁺ ions, so it is believed that the glassy network is strengthened, and that the Fe³⁺ ion is located in tetrahedral or octahedral sites and acts as a network former [16,17]. Also, it was determined that both oxidation states have good chemical durability in P–O–Feⁿ⁺ bonds [16]. Therefore, it is expected that the water resistance of phosphate

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Table 1. Chemical compositions and thermal properties of P_2O_5 -ZnO- Bi_2O_3 - xFe_2O_3 glass samples.

Sample	P_2O_5	ZnO	Bi_2O_3	Fe_2O_3	T_g	T_s	CTE
	(mol-%)				(°C)		($10^{-7} K^{-1}$)
S1	50.0	30.0	20.0	0.0	428.04	465.84	95.7
S2	49.0	29.4	19.6	2.0	433.63	505.2	78.33
S3	48.1	28.8	19.2	3.8	441.98	517.98	73.74
S4	47.2	28.3	18.9	5.7	469.02	541.17	72.76
S5	46.3	27.8	18.5	7.4	481.86	556.09	70.41
S6	45.5	27.3	18.2	9.1	488.01	570.33	70.76

glass can be improved by increasing the number of Fe-O-P bonds.

In this study, Fe_2O_3 was added to the P_2O_5 -ZnO- Bi_2O_3 ternary glass system to improve its water resistance. The mass loss in water, thermal properties, and wetting properties of the sealing glass were investigated.

2. EXPERIMENT PROCEDURES

2.1. Glass preparation

In this study, P_2O_5 -ZnO- Bi_2O_3 (PZBi20) was selected from the authors' previous study as a starting composition [2]. Table 1 shows the material composition of $50P_2O_5$ - $30ZnO$ - $20Bi_2O_3$ - xFe_2O_3 (mol%) (where $x = 0, 2, 4, 6, 8$, and 10). All materials were high purity $NH_4H_2PO_4$, ZnO, Bi_2O_3 (99%), and Fe_2O_3 (98%) from Junsei Chemical Co., Ltd. The raw materials were mixed in an alumina container with manual shaking for 10 min and then melted at 1200 °C for 1 h in air condition. The melt was poured onto a stainless steel substrate at room temperature. The glasses were annealed at their glass transition temperature for 1 h. Prior to X-ray diffraction (XRD), Fourier transfer infrared spectroscopy (FT-IR) and wetting property analyses, the glass powder was passed through a 325 mesh sieve. The powder was kept in a vacuum desiccator to prevent moisture absorption.

2.2. Measurement

2.2.1 Identification and verification

Quenched glass samples were inspected to determine their level of crystallization. Using X-ray diffraction (XRD) analysis (Rigaku Corporation/Cu/30 kV/15 mA), the existence of a

crystalline phase was investigated.

2.2.2 Structural property

FTIR (Spectrum GX, 400–1600 cm^{-1}) was used to observe the structural change resulting from the addition of Fe_2O_3 . The fine glass powder was mixed with highly pure KBr powder at a 200:1 ratio and dried at 100 °C. The mixtures were pressed into thin disc to record the spectra.

2.2.3 Thermal properties

The thermal properties of glass transition temperature (T_g), softening temperature (T_s) and the coefficient of thermal expansion (CTE) were measured using a thermal mechanical analyser (Q-400 TMA, T.A. Co, USA). The heating rate was 10 °C min^{-1} and the temperature range was 25–650 °C. Using a sample size of 5 g, the measurements from three samples were averaged.

2.2.4 Water resistance

To evaluate the glass samples' thermal properties and water resistance, they were cut into $0.5 \times 0.5 \times 0.5$ cm^3 specimens and placed into distilled water at 90 °C for 96 h. Weight loss was measured using an electronic scale (AND Co., GH-200, $d = \pm 0.001$ g). The weight loss value was calculated by weight loss value (g) / surface area (cm^2). Also, the data results were the average value of three tests.

2.2.5 Wetting property

Cylindrical pellets were made with 0.2 g of each of the glass powder samples. The contact angle between the pellet-air surface and substrate (low carbon steel) was measured using hot stage microscopy. The disc pellets were

Fig. 1. XRD patterns of the P_2O_5 -ZnO- Bi_2O_3 - xFe_2O_3 glass samples.

heated from 25 °C to 850 °C at a heating rate of 10 °C min⁻¹ in ambient air. The temperature range used for measuring the contact angle was 650–850 °C.

3. RESULTS AND DISCUSSION

3.1. Identification and verification

As seen in Figure 1, the XRD patterns for all samples indicate the formation of glass. At S6 sample, the little crystalline phase was inspected. However, the peak intensity was lower than 200(cps) and in optical microscope test which inspected glass surface showed having no crystalline phase. Thus, we have tested about each property including S6 sample.

3.2. Structural property

Figure 2 shows the FTIR graph of each of the 50P₂O₅-30ZnO-20Bi₂O₃- xFe_2O_3 ($x = 0, 2, 4, 6, 8$, and 10 mol%) glass samples (S1 through S6) over 400–1400 cm⁻¹. The bands characteristic of Fe-O-P bonds are seen at 510 cm⁻¹, and this peak increased with increasing additions of Fe₂O₃ [16,18]. Peak intensity increased linearly from sample S4 and peaked at sample S6, which was doped with 10 mol% Fe₂O₃.

The symmetric and asymmetric stretching vibrations of the P-O-P bonds are related to 760 and 925 cm⁻¹, respectively [17,19-21]. The peak of the P-O-P symmetric band increased as the concentration of Fe₂O₃ from 0 mol% to 10 mol%. This

Fig. 2. FTIR spectra of the P_2O_5 -ZnO- Bi_2O_3 - xFe_2O_3 glass samples.

means that the number of P-O-P bonds decreased with increasing Fe₂O₃.

The region at approximately 460 cm⁻¹ vibration is related to the Bi-O bonds of the BiO₆ structure [22]. In this region, the peak increased as the level of Fe₂O₃ increased. It can be concluded that the number of Bi-O bonds decreased with increasing Fe₂O₃. As a result, the addition of Fe₂O₃ caused a decrease in the number of P-O-P and Bi-O-P bonds, while causing an increase in the number of Fe-O-P bonds. Therefore, it is expected that FeO₆ groups which contain Fe²⁺ and Fe³⁺ ions are formed by the addition of Fe₂O₃, constituting a structure interconnected via (P₂O₇)⁴⁻ groups within the glass network [16,23]. By considering the effect of this phenomenon, the thermal properties, wetting properties and water resistance can be explained.

3.3. Thermal properties

The thermal properties of samples S1 through S6 are presented in Table 1 and Fig 3. T_g and T_s increased linearly with increasing Fe₂O₃. Sample S1 had the lowest T_g and T_s , at 428.04 °C and 465.84 °C, respectively, whereas S6 had much higher values for T_g (488.01 °C) and T_s (570.33 °C). The CTE values decreased with increasing Fe₂O₃.

There was a rapid decrease in CTE between S1 and S2 of $17.37 \times 10^{-7} K^{-1}$. From sample S2 to S6, the decrease in CTE was less significant. This means that the thermal expansion

Table 2. Contact angles of P_2O_5 - ZnO - Bi_2O_3 - xFe_2O_3 glass samples from 650 to 850 °C

	650 °C	700 °C	750 °C	800 °C	850 °C
S1	128.5°	116.2°	110.7°	94.3°	42.6°
S2	95.3°	101.6°	117.6°	95.9°	50.8°
S3	95.0°	100.5°	116.3°	98.2°	54.4°
S4	94.1°	98.3°	115.0°	101.1°	57.0°
S5	92.3°	97.4°	108.3°	104.5°	59.2°
S6	90.5°	95.0°	119.0°	110.7°	64.1°

Fig. 3. Thermal properties of the P_2O_5 - ZnO - Bi_2O_3 - xFe_2O_3 glass samples.

was lower with increases in Fe_2O_3 and the glass structure was strengthened with the addition of Fe_2O_3 due to the formation of Fe-O-P bonds. These Fe-O-P bonds created a cross-linked structure between the phosphate groups, resulting in a more rigid glass structure. In addition, it can be reasoned that the number of Bi-O-P bonds, which are weak compared with the Fe-O bonds, decreased with increasing Fe_2O_3 .

3.4. Water resistance

Figure 4 shows the weight loss for 1cm^2 of the glass samples as a function of the Fe_2O_3 level. S1 had the highest weight loss ($1.710 \times 10^{-2} \text{ g cm}^{-2}$), at 96 h) and S6, which had the highest level of Fe_2O_3 , had the lowest weight loss ($0.514 \times 10^{-2} \text{ g cm}^{-2}$), at 96 h). It is interesting to note that the slopes of the weight loss lines for S1, S2 and S3 are higher than those for S4, S5, and S6. It can be concluded that the addition of Fe_2O_3 influences the water resistance of the glass. The existing P-O-P and Bi-O-P bonds of the bismuth-phosphate composition glass have been replaced with Fe-O-P bonds by

Fig. 4. Weight loss of the P_2O_5 - ZnO - Bi_2O_3 - xFe_2O_3 glass samples over 96 h. **Fig. 5.** Contact angles of the P_2O_5 - ZnO - Bi_2O_3 - xFe_2O_3 glass samples from 650 to 850 °C.

the addition of Fe_2O_3 . As a result, the addition of Fe_2O_3 improves the water resistance of the glass.

3.5. Wetting properties

Each glass has a respective wetting property and this is an important characteristic for sealing work in different environments. Table 2 and Fig. 5 show the angle between the pellet-air surface and the substrate with respect to time. Most samples, except the S1 sample, showed a wetting angle increasing to 750 °C and decreasing to 850 °C. This phenomenon is explained with sintering behaviour: the highest contact angle occurs when the glass powder pellet is shrunk, and above the shrinkage temperature, the pellet

collapsed and showed wetting phenomenon [24].

S1 had a large angle and appeared highly deformed at 650 °C (128.5°). Over time, the contact angle decreased with temperature, and reached its lowest point at 850 °C (42.6°). On the other hand, samples S2 through S6, which were Fe₂O₃-doped, deformed at a slower rate than that of S1 and peaked at 750 °C. At 700 °C, S6 had the highest contact angle, but at 800 °C, it had the lowest among all the samples. Typically, Fe₂O₃-doped glasses show a greater contact angle, compared with undoped glasses at temperatures less than 750 °C. At 850 °C, the contact angles increased linearly as a function of the Fe₂O₃ level and S6 had a contact angle that was 21.5° greater than that of S1. These results indicate that the glass is reinforced with the addition of Fe₂O₃. The addition of Fe₂O₃ causes an increase in T_s, which makes the glass structure more rigid. Because stronger glass is more stable at high temperatures, less deformation occurs when the glass is Fe₂O₃ doped than when it is undoped.

4. CONCLUSIONS

The characteristics of a Fe₂O₃ doped P₂O₅-ZnO-Bi₂O₃ ternary glass system were analysed. By adding Fe₂O₃ into phosphate glasses, P-O-P bonds and Bi-O-P bonds were replaced with Fe-O-P bonds. As a result, it is expected that a stronger glass network was formed by the Fe²⁺ and Fe³⁺ ions, which induced the formation of a network structure within glass. Because of the strengthened glass network, the glass structure was strengthened. This was proven by the increased T_d and T_s, and the decreased CTE. In addition, through water resistance analysis, the Fe₂O₃-doped glass was shown to be more durable than undoped glass. Also, the wetting property analysis indicated a larger contact angle with an increasing level of Fe₂O₃, due to the higher T_s and the rigid structure.

ACKNOWLEDGMENT

This work was supported by the Korea Institute of Energy

Technology Evaluation and Planning(KETEP) and the Ministry of Trade, Industry & Energy(MOTIE) of the Republic of Korea (No. 20151520302060).

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