Effects of Bi$_2$O$_3$ on the structural, thermal and wetting properties of zinc bismuth phosphate glasses for low-melting sealing glass

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The study of lead-free low-melting sealing glass with properties such as low glass transition temperature ($T_g$), low softening temperature ($T_s$), and good wettabity on the substrate, is in process. One of the low-sintering lead-free glass compositions, the bismuth glass system is considered to be an alternative to lead oxide glass. Research on the development of lead-free low-melting sealing glass in ZnO–P$_2$O$_5$–Bi$_2$O$_3$ (ZPB) system was prepared and the effects of substitution of Bi$_2$O$_3$ for ZnO on the structural, thermal, and wetting properties of a sealing glass were studied. The changes in $T_g$, $T_s$, and coefficient of thermal expansion (CTE) may reflect decreasing connectivity of the glass structure, due to the increasing Bi–O bonds. This structure changes have an effect on wettability on the substrate. The addition of higher amounts of Bi$_2$O$_3$ improved the wettability of the glass on the substrate. The ZPB glass, possessing properties of low $T_g$ and good wettability, is suitable for low-to-mid temperature sealing applications.

Key-words : Sealing, ZnO–P$_2$O$_5$–Bi$_2$O$_3$ glass, Glass structure, Thermal properties, Wettability

1. Introduction

Phosphate glasses have often been spotlighted owing to their superior physical properties to other glasses, such as a high thermal expansion coefficient, low melting temperature, and softening temperature. These properties make them a candidate material for important applications such as sealing. Sealing glass is widely used for the sealing of various kinds of electronic applications such as sensors, color televisions, PDP. However, phosphate glasses have poor chemical durability, and so, find limited applications. In order to solve this problem, several researchers have reported adding various oxides to chemical durability of phosphate glasses. Also, given the recent environmental regulations, research on lead-free electronic packaging has gained importance. The oxides used to replace PbO are V$_2$O$_3$, SnO$_2$, and Bi$_2$O$_3$. According to a previous study, the role of Bi$^{3+}$ in glasses may be compared to that of Pb$^{2+}$, because Bi$^{3+}$ has properties similar to Pb$^{2+}$, such as atomic weight, ionic radius, and electronic configuration. Using these characteristics of Bi$_2$O$_3$, Optical property of Zinc bismuth phosphate glass used in this study according to Bi$_2$O$_3$ contents have been studying. Also, the group of the authors has researched correlation between glass structure and properties in Zno–P$_2$O$_5$–Bi$_2$O$_3$ glass system in 2009 and 2010, and examined the relationship of thermal, optical, property with the structure. Meanwhile, one of the important factors for a sealing glass is its flow properties at the sealing temperature, especially the glass wettability on the sealing surface. In the previous study, however the studies about wettability on the substrate have not been carried out. Therefore, in this study, to confirm the sealing glasses, we investigated the effect of Bi$_2$O$_3$ content on the thermal, physical behavior of lead-free low- melting ZnO–P$_2$O$_5$–Bi$_2$O$_3$ glasses, as well as their structure, and the relation of the wetting angle to the sealing temperature was studied.

2. Experimental method

Glasses having the composition (50 – x)ZnO–50P$_2$O$_5$–xBi$_2$O$_3$, with x = 0–20 mol % were prepared for our study. A ZPB glass was prepared from high-purity ZnO (98%), Bi$_2$O$_3$ (99.9%), and NH$_4$H$_2$PO$_4$ (99.9%). All materials were purchased from Junsei Chemical Co. (Tokyo, Japan). The raw materials were mixed by manual shaking for 5 min, melted at 1200°C, and kept at the melting temperature for 1 h. The molten glass was then quenched by pouring it on a stainless steel plate. The obtained glasses were annealed at the glass transition temperature, $T_g$, for 1 h, cut, and mechanically polished to obtain samples for thermal and chemical analysis. The thermal properties of the glasses were investigated using a Thermal Mechanical Analyzer (TMA, Q400, TA Instruments), working in the temperature range from room temperature to 600°C at heating rates of 10°C/min. The thermal properties values were determined for each glass using the associated computer software and the accuracy of the measurement is ±2°C based on the average of 3 replicates. The density ($\rho$) of the glasses was examined using the Archimedes method (Using AND GH-200). To get the Fourier transform infrared (FT-IR) absorption spectra of the glass sample, the KBr pellet technique was employed. The glass samples were ground to a fine powder and a weighed quantity (0.001 g) of the powder was thoroughly mixed with desiccated, highly purified (99.99%) KBr powder (0.1 g). The mixture was pressed into thin pellets in order to record the spectra. The contact angle measurements were performed on the glass samples using an automatic hot-stage microscope (HSM, H.Lab Co, Korea). The measurement was taken in air at heating rate of 10°C/min. The samples of for these measurements were made using a hand press compress the glass frits (0.1 g), which were putted within a small cylindrical metal mold (10 mm × 10 mm). A sample image automatically recorded and analyzed the sample geometry during heating process. An alumina plate (20 mm × 20 mm × 0.7 mm) was used as the substrate.

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3. Result and discussion

The effect of the substitution of Bi$_2$O$_3$ for ZnO on the density of the glasses is shown in Fig. 1. The density of the glasses increased slightly with increasing Bi$_2$O$_3$ content (Fig. 1 and Table 1). This phenomenon is explained by the fact that the heavy metal oxide, Bi$_2$O$_3$, replaces the relatively lighter oxide (ZnO). The molar volume of the glasses is given by $V_M = M/\mu$.

The values of the molar volume, $V_M$, calculated from the values of the density, can be seen from Table 1 and Fig. 1. The molar volume of the glasses increases with increasing content of Bi$_2$O$_3$. This was expected, as the addition of Bi$_2$O$_3$ depolymerizes the phosphate chains and forms P–O–Bi bonds, bonds that are more longer than the P–O–Zn bonds due to the higher ionic radius of Bi$^{3+}$ (0.102 nm) than that of Zn$^{2+}$ (0.074 nm). This depolymerization may cause an increase in molar volume.

The effect of substitution of Bi$_2$O$_3$ for ZnO on the thermal properties of the glasses is shown in Fig. 2. The thermal property of the glasses is correlated with their composition and structure. There is a monotonic change in both $T_g$ and $T_s$. The $T_g$ decreases with increasing Bi$_2$O$_3$ content, from 460 to 425°C, when the Bi$_2$O$_3$ content increases from 0 to 20 mol %. The $T_s$ too decreases with increasing Bi$_2$O$_3$ content, from 502 to 460°C, when the Bi$_2$O$_3$ content increases from 0 to 20 mol %. The rate of change is greater for Bi$_2$O$_3$ > 10 mol %, these slope changes are related to glass structure. With further addition of Bi$_2$O$_3$(≥10 mol %), the Bi–O–P bond was formed in the glass matrix, which will be further explained by the following FT-IR analysis. Figure 2 also shows the effects of the Bi$_2$O$_3$ content on the CTE of the glasses. The CTE of the glasses increases with increasing Bi$_2$O$_3$ content, from 64.8(10$^{-7}$/K) to 95.1(10$^{-7}$/K), when the Bi$_2$O$_3$ content increases from 0 to 20 mol %. These phenomena can be explained by the Bi$_2$O$_3$ acting as a glass modifier. The bismuth ions disrupt the glass network and lower its. Therefore, the increase in CTE and the decrease in $T_g$ and $T_s$ with increasing Bi$_2$O$_3$ content may be because of the increase in the number of non-bridging oxygens (NBOs).

Figure 3 demonstrates the FT-IR spectra of the glasses over the range 400–1400 cm$^{-1}$. The bands characteristic of P–O–P bridges at about 925 and 790 cm$^{-1}$ are attributed to the existence of pyrophosphate units, and specifically to the asymmetric and symmetric stretching vibrations of the P–O–P bonds, respectively. With increasing Bi$_2$O$_3$ content, and the consequent decrease in ZnO content, the spectra of the glasses were changed. With the addition of 5 mol % Bi$_2$O$_3$, the intensity of the PO$_2$ symmetric stretching band decreases, and its corresponding band shifts towards a lower frequency (from 1220 cm$^{-1}$). This phenomenon can be explained by the decondensation of Zn(PO$_3$)$_2$ by Bi$^{3+}$ ions, resulting in the formation of short chain phosphates. The average phosphate chain length becomes shorter as the O/P increases. The higher the amount of Bi$_2$O$_3$, the O/P increases.

![Fig. 1. Density & Molar volume ZPB glass as function of Bi$_2$O$_3$ contents.](image1)

![Fig. 2. Thermal properties of the ZPB glass as a function of Bi$_2$O$_3$ contents.](image2)

![Fig. 3. FT-IR spectra of the ZPB glass as a function of Bi$_2$O$_3$ contents.](image3)

### Table 1. Physical and Thermal properties of ZPB glasses

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZnO (mol %)</th>
<th>Bi$_2$O$_3$ (mol %)</th>
<th>P$_2$O$_5$ (mol %)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$V_M$ (cm$^3$)</th>
<th>$T_g$ (°C)</th>
<th>$T_s$ (°C)</th>
<th>CTE (10$^{-5}$/K)</th>
<th>O/P</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZPB0</td>
<td>50</td>
<td>0</td>
<td>50</td>
<td>2.886</td>
<td>38.67</td>
<td>460</td>
<td>502</td>
<td>64.8</td>
<td>3.0</td>
</tr>
<tr>
<td>ZPB5</td>
<td>45</td>
<td>5</td>
<td>50</td>
<td>3.371</td>
<td>38.81</td>
<td>457</td>
<td>492</td>
<td>72.6</td>
<td>3.1</td>
</tr>
<tr>
<td>ZPB10</td>
<td>40</td>
<td>10</td>
<td>50</td>
<td>3.751</td>
<td>40.00</td>
<td>437</td>
<td>473</td>
<td>78.9</td>
<td>3.2</td>
</tr>
<tr>
<td>ZPB15</td>
<td>35</td>
<td>15</td>
<td>50</td>
<td>4.095</td>
<td>41.34</td>
<td>433</td>
<td>463</td>
<td>84.5</td>
<td>3.3</td>
</tr>
<tr>
<td>ZPB20</td>
<td>30</td>
<td>20</td>
<td>50</td>
<td>4.400</td>
<td>42.84</td>
<td>425</td>
<td>460</td>
<td>95.1</td>
<td>3.4</td>
</tr>
</tbody>
</table>
from 3.0 to 3.4 (Table 1), so the phosphate chain length becomes shorter. The higher the amount of Bi$_2$O$_3$ ($\geq$ 10 mol %), the weaker the PO$_2$ symmetric band at 1220 cm$^{-1}$ becomes, shifting towards a lower frequency. With more than 15 mol % Bi$_2$O$_3$, the PO$_2$ symmetric band disappears. This indicates that (PO$_2$)$_n$ chains do not remain in this glass system, and it is assumed that PO$_3$ chains are formed instead. The stretching vibration of the PO$_3$ group is attributed to the Bi-O-P bonds. 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. 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. 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. Moreover, the frequency of the (P–O–P)$_n$ groups (925 cm$^{-1}$) increases upon Bi$_2$O$_3$ addition. This is to be expected given the presence of pyrophosphate groups and that the frequency of the (PO$_2$)$_n$ groups shift towards a lower wave number as a consequence of Bi$_2$O$_3$ addition. The intensity of the band at 1105 cm$^{-1}$ is not changed when compared to the intensity of the asymmetric stretching vibration of P–O–P bonds at 925 cm$^{-1}$. This phenomenon is attributed to the asymmetric stretching vibration of the PO$_3$ groups in the short phosphate chains. It was observed that the main bands of glasses ZPB5–ZPB20 were broader than that of glasses ZPB0, indicating that the glass network became looser while ZnO was replaced by Bi$_2$O$_3$. This might be due to the conversion of BO$_3$s (bridging oxygens) into NBO$_3$s (Non-bridging oxygens).

Good wettability is one of the most important factors influencing favorable adhesion. The pellet shape of the glass with increasing temperature is represented in Fig. 4; the pellets are initially square shaped (Region I). With increasing temperature, the pellet shape changes from square to spherical. The formation temperature of the swollen sphere is known as the softening point. Heat energy first reacted at the corner due to the largest surface area. So, the corner of the pellet contract rapidly to reduce surface energy. At higher temperatures (> $T_s$), the shape of the pellet changes to an ellipsoid shape (Region II), and the molten glass spreads over the substrate (Region III). The wetting behavior of the glasses on low-carbon steel substrate was studied for the substitution of Bi$_2$O$_3$ for ZnO shown in Fig. 5. The wetting angle of the ZPB0 glass was maintained at 90°C from room temperature to 510°C. Above 510°C, this glass starts wetting the substrate. The higher the amount of Bi$_2$O$_3$, the starting temperature of swollen sphere was decreased (Figs. 4 and 5). Generally, the wetting behavior of the glasses containing Bi$_2$O$_3$ was better than that of ZPB0 glass. Furthermore, the addition of higher amounts of Bi$_2$O$_3$ improved the wettability of the glass on the substrate at same temperature. At 850°C, the value of wetting angle of ZPB20 composition appears 39.6°. This phenomenon is closely related to glass structure. The FT-IR analysis showed the conversion of BO$_3$s into NBO$_3$s by the substitution of Bi$_2$O$_3$ for ZnO. Consequently, the glass network weakened and the glass flowed easily, which improved glass wettability.
4. Conclusion

In this study, to consider the lead-free low-melting sealing material of the ZnO-P₂O₅-B₂O₃ glass, the effects of the substitution of Bi₂O₃ for ZnO on the structural, thermal, and wetting properties of ZPB glasses were studied. ZPB glass included with high amount Bi₂O₃ appears low Ts,Tg high CTE. Such thermal properties change is highly related to the change of the glass structure. With further addition of Bi₂O₃, the connectivity of the glass structure decreases, due to the increasing Bi-O bonds. Consequently, the glass network weakened and the glass flow easily. Also, this structure change is judged main factor of wettability between the glass frit and substrate. The ZPB glass composition of the high amounts of Bi₂O₃ improved the wetting ability on the substrate. At 850°C, the value of wetting angle of ZPB20 composition appears 39.6°. The ZPB glass system with high Bi₂O₃ gives low thermal properties, high wetting ability, making it a potential alternative to current commercial sealing glass. The authors hope that the information obtained in this study will be helpful in investigating the sealing materials of Bi₂O₃-containing glasses.

References