Various glasses with different compositions \((50 - 2x)\text{ZnO} - x\text{Bi}_2\text{O}_3 - (50 + x)\text{P}_2\text{O}_5\) \((x = 0 \sim 20 \text{ mol\%})\) were prepared. This study examined the effect of the structure and properties in phosphate glass system according to the change in \(\text{Bi}_2\text{O}_3\) content in \(\text{ZnO- Bi}_2\text{O}_3- \text{P}_2\text{O}_5\) glass. The structure of the glasses was analyzed by Fourier transform infrared (FT–IR) analysis. The FTIR spectra were recorded in the spectral range from 400 to 1400 cm\(^{-1}\). The structural investigations based on these spectra showed the rapid depolymerization of the phosphate chains with increasing \(\text{Bi}_2\text{O}_3\) content along with the formation of \(\text{P-O-Bi}\) bonds. The density, glass transition temperature (\(T_g\)), molar volume and optical properties of the glasses were determined from the structural changes in the glasses. \(T_g\), density and molar volume increased with increasing in \(\text{Bi}_2\text{O}_3\) content in the glass. The optical absorption edge (\(\lambda_{\text{cut-off}}\)) and optical band gap (\(E_g\)) were determined from the optical transmittance spectra of the polished samples recorded at room temperature, and found to be associated with structural changes occurring in these glasses with increasing \(\text{Bi}_2\text{O}_3\) content.

1. Introduction

Phosphate glasses are both scientifically and technologically important materials on account of their superior physical properties to other glasses, such as high thermal expansion coefficient, low melting and softening temperatures, high electrical conductivity, ultraviolet (UV) transmission and optical characteristics. These properties make them useful candidates for fast ion conducting materials and other important applications, such as laser hosts, glass-to-metal seals and bio-compatible materials. Phosphate glasses have unique properties that make them useful for a wide range of technical applications. However, these glasses have a relatively poor chemical durability, which often limits their usefulness. Several studies have reported that the chemical durability of phosphate glasses can be improved by the addition of various oxides. The physical properties and chemical durability of alkali phosphate glasses can be improved by adding oxides of high valance cations, such as \(\text{Al}^{3+}\), \(\text{Ti}^{4+}\), \(\text{Bi}^{3+}\), etc. as these form relatively stable \(\text{M}^{4+-}\text{O-P}\) cross-linked bonds. It was reported that \(\text{Bi}_2\text{O}_3\) occupies both network-forming and network-modifying positions in oxide glasses. Therefore, the physical properties of glass containing \(\text{Bi}_2\text{O}_3\) exhibit discontinuous changes when the structural role of the cation is switched in this manner. In addition, these glasses have attracted a considerable attention because of their wide applications in the field of glass ceramics, thermal and mechanical sensors, reflecting windows as well as their potential use as layers for optical and optoelectronic devices.

Studies of \(\text{Na}_2\text{O- CuO- Bi}_2\text{O}_3 - \text{P}_2\text{O}_5\) quaternary glasses\(^{8,9}\) reported that the addition of \(\text{CuO}\) or \(\text{Bi}_2\text{O}_3\) increase the glass transition temperature and depolymerize phosphate chains. According to Chahine et al.,\(^{10}\) the \(\text{Bi}_2\text{O}_3\) in these glasses behaves as a network former and is incorporated in the network as \(\text{BiO}_6\) units. This study examined the effects of the \(\text{Bi}_2\text{O}_3\) content on the physical and optical properties as well as the structure of \(\text{ZnO- Bi}_2\text{O}_3- \text{P}_2\text{O}_5\) glasses, as a metaphosphate structure glass. The relationship between the local structure and physical properties around the bismuth ions is discussed.

2. Experimental procedure

2.1 Preparation of glass sample

Glasses with a composition of \((50 - 2x)\text{ZnO} - x\text{Bi}_2\text{O}_3 - (50 + x)\text{P}_2\text{O}_5\) \((x = 0 \sim 20 \text{ mol\%})\) were prepared. The glasses were prepared from reagent grade \(\text{ZnO}, \text{Bi}_2\text{O}_3\) and \(\text{NH}_4\text{H}_2\text{PO}_4\). Well mixed batches calculated to yield 50 g of glass were melted in an alumina crucible for 1 h at 1200°C. The glass melt was quenched by pouring on a stainless plate. The glasses obtained were annealed at the glass transition temperature, \(T_g\), for 30 min, and then, cut and mechanically polished to obtain the samples for thermal and chemical analysis. The glass samples were polished to optical quality for the optical measurements. The sample thickness ranged from 0.5 to 1.5 mm. The KBr pellet technique was employed to obtain the Fourier transform infrared (FT–IR, Bruker IFS66 Germany) absorption spectra of a glass sample. The glass samples were ground to a fine powder and a weighed quantity (0.001 g) of the powder was mixed intimately with a specified quantity of KBr powder. The mixture was pressed in the thin pellets in order to record the spectra.

2.2 Measurements

The thermal behavior of the glasses was examined using a TMA–50 (Shimadzu Co.), working in the temperature range of 25–1000°C at heating rates of 10 K/min. The density, \(\rho\), of the sample was measured using the Archimedes method using the Archimedes method (using AND GH–200). The molar volume \(V_M\) was calculated as \(V_M = M/\rho\),
where $\overline{M}$ is the average molar weight of the glass composition, $x\text{ZnO} - y\text{Bi}_2\text{O}_3 - z\text{P}_2\text{O}_5$ calculated for $x + y + z = 1$. The absorption spectra of the glasses were measured by ultraviolet/visible spectroscopy (UV-vis, Agilent 8453). The cut-off wavelength was determined from the absorption spectra. The structure of the glasses was analyzed by FTIR spectroscopy.

3. Results and discussion

3.1 Density and molar volume

Table 1 lists the density ($\rho$) of all the glass samples. The density increased with increasing Bi$_2$O$_3$ content in the glass systems. This was expected as the heavy metal oxide (Bi$_2$O$_3$) replaces the lighter oxides (ZnO). Figure 1 shows the change in the density and molar volume with Bi$_2$O$_3$ content for the glass. The molar volume of glasses is given by

$$V_M = \frac{\overline{M}}{\rho}$$

where $\overline{M}$ is the average molar weight of the glass composition, $x\text{ZnO} - y\text{Bi}_2\text{O}_3 - z\text{P}_2\text{O}_5$ calculated for $x + y + z = 1$, and $\rho$ is the density. The molar volume, $V_M$, of the (50 – 2$x$)ZnO–$x$Bi$_2$O$_3$–(50 + $x$)P$_2$O$_5$ glasses increased almost linearly with increasing Bi$_2$O$_3$ content, whereas the recently reported molar volume of lithium bismuth phosphate glasses decreased with increasing Bi$_2$O$_3$ content. In this study, the structure of the base glass was characterized by the metaphosphate chains. The addition of Bi$_2$O$_3$ depolymerizes the phosphate chains and forms P–O–Bi bonds. These P–O–Bi bonds are more ionic and longer than the P–O–Zn bonds, and may cause an increase in molar volume. The decrease in molar volume in lithium bismuth phosphate glasses with increasing Bi$_2$O$_3$ content was explained by the formation of Bi–O bonds.

3.2 Glass transition temperature

Figure 2 shows the glass transition temperature, $T_g$, of the glasses at different Bi$_2$O$_3$ contents. Table 1 shows the change in $T_g$ with composition for the glass system. $T_g$ decreased with the addition of 5 mol% of Bi$_2$O$_3$ in the glass matrix, which might be due to the decondensation of phosphate chains. With further addition of Bi$_2$O$_3$ to the system, $T_g$ increased slightly from 451 to 461°C. The reported $T_g$ for the lithium bismuth phosphate glass is lower than the $T_g$ determined in the present glasses corresponding to same Bi$_2$O$_3$ composition. This was expected because Zn–O and P–O–Zn bonds are formed in the glass matrix, which would have more covalent character than Li–O and P–O–Li bonds. Also coefficient of Thermal Expansion (CTE) increased with the addition of Bi$_2$O$_3$.

3.3 Optical properties

Figure 3 shows the optical transmittance spectra of the trivalent ZnO–Bi$_2$O$_3$–P$_2$O$_5$ glasses in the visible and near UV range. There was no sharp absorption edge, which is characteristic of a glassy state. The position of the cut-off wavelength shifted to a higher energy with increasing Bi$_2$O$_3$ content in trivalent ZnO–Bi$_2$O$_3$–P$_2$O$_5$ glasses. The absorption coefficient, $\alpha$, below and above $\lambda_{cut-off}$.

Table 1. Density, Molar Volume, Glass Transition Temperature, Coefficient of Thermal Expansion (CTE), Cut-Off Wavelength, Optical Band Gap ($E_g$) and O/P Ratio of ZnO–Bi$_2$O$_3$–P$_2$O$_5$ Glasses

<table>
<thead>
<tr>
<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>CTE ($10^{-5}$/K)</th>
<th>$\lambda_{cut-off}$ (nm)</th>
<th>$E_g$ (eV)</th>
<th>O/P</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0</td>
<td>50</td>
<td>2.886</td>
<td>38.691</td>
<td>460</td>
<td>65</td>
<td>190</td>
<td>5.85</td>
<td>3.0</td>
</tr>
<tr>
<td>40</td>
<td>5</td>
<td>55</td>
<td>3.229</td>
<td>41.473</td>
<td>451</td>
<td>74.2</td>
<td>291</td>
<td>4.00</td>
<td>3.0</td>
</tr>
<tr>
<td>30</td>
<td>10</td>
<td>60</td>
<td>3.487</td>
<td>44.793</td>
<td>454</td>
<td>86</td>
<td>294</td>
<td>3.95</td>
<td>3.0</td>
</tr>
<tr>
<td>20</td>
<td>15</td>
<td>65</td>
<td>3.719</td>
<td>47.984</td>
<td>458</td>
<td>91.9</td>
<td>296</td>
<td>3.92</td>
<td>3.0</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>70</td>
<td>3.922</td>
<td>51.171</td>
<td>461</td>
<td>125.7</td>
<td>299</td>
<td>3.88</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Fig. 1. Density and molar volume of the LBP and ZBP glasses as a function of the batched Bi$_2$O$_3$ content.

Fig. 2. Glass transition temperature and Coefficient of Thermal Expansion (CTE) of ZnO–Bi$_2$O$_3$–P$_2$O$_5$ glasses as a function of the batched Bi$_2$O$_3$ content.

Fig. 3. Optical transmittance spectra of (50 – 2$x$)ZnO–$x$Bi$_2$O$_3$–(50 + $x$)P$_2$O$_5$ ($x = 0–20$) glasses.
near the edge of each curve was calculated using Lambert’s law as follows:

\[ a = \frac{1}{d} \ln(\frac{I}{I_0}) \]  

(2)

where \( t \) is the sample thickness and \( T \) is the transmittance. The optical band gap of ZBP glasses was estimated by extrapolating the linear portion of \((ahv)^{1/2} \) versus \( hv \) plots using the following relation:

\[ ahv = \alpha(E_h - E_g)^{1/2} \]  

(3)

where \( \alpha \) is the absorption coefficient, \( hv \) is the photon energy, \( A \) is a constant and \( E_g \) is the optical band-gap energy. For amorphous materials, indirect transitions \((r = 2, 3)\) are valid according to the Tauc’s relations.\(^{12}\) Figure 4 presents the change in \((ahv)^{1/2} \) vs. \( hv \) (Tauc’s plot) for ZBP glasses. \( E_g \) can be obtained (using Eq.(3)) by extrapolating the linear region of the curves in Fig. 4 to \((ahv)^{1/2} = 0 \).\(^{12}\) The results are given in Table 1. The decrease in \( E_g \) with increasing \( \text{Bi}_2\text{O}_3 \) content of the transitions (Table 1) corresponds to the red shift in \( \lambda_{\text{cut-off}} \). This suggests that the non-bridging oxygen (NBO) ions increasing with increasing \( \text{Bi}_2\text{O}_3 \) concentration. An increase in the concentration of NBO ions resulted in a shift of the VBM to higher energies, which reduced the band gap.

### 3.4 FT–IR analysis

Figure 5 shows the FTIR spectra of the glass systems over the frequency range, 400–1400 cm\(^{-1}\). According to Brow,\(^{13}\) for binary glasses \( x\text{R}_2\text{O}\cdot(1-x)\text{P}_2\text{O}_5 \) (\( \text{R}_2\text{O} \): alkali oxide), the network is based on \( Q_3 \) and \( Q_2 \) units in the ultraphosphate region \((0 \leq x < 0.5)\); whereas in metaphosphate glasses \((x = 0.5)\), the network is based entirely on the \( Q_2 \) tetrahedra, which forms chains and rings. These chains and rings are linked by more ionic bonds between the various metal cations and nonbridging oxygen atoms. The characteristic features of the glass spectrum for \( x = 0 \) [\( \text{Zn}(\text{PO}_3)_2 \) glass] of the glass system (Fig. 5) were the \( \text{PO}_2 \) asymmetric stretching vibration band at 1265 cm\(^{-1}\), the \( \text{PO}_2 \) symmetric stretching band at 1220 cm\(^{-1}\), the \( \nu \) of \( \text{P}–\text{O}–\text{P} \) groups (chain terminators) at 1105 and 1005 cm\(^{-1}\), the \( \nu \) of POP groups at 925 cm\(^{-1}\), the \( \nu \) of POP groups at 755 cm\(^{-1}\) and the deformation modes of \( \text{P}–\text{O} \) \((\text{PO}_3^3)\) groups at 480 cm\(^{-1}\).\(^{14}\) The simultaneous occurrence of the two bands characteristic of the \( \text{P}–\text{O}–\text{P} \) bridge at 925 and 755 cm\(^{-1}\), respectively, may be a good indication of the existence of pyrophosphate units.\(^{15}\) For the glass sample, the intensity of \( \text{P}–\text{O}^– \) groups at 1105 and 1005 cm\(^{-1}\) indicates the presence of some \( Q_3 \) units in the glass sample. For the glass sample, there was decrease in the intensity of a \( \text{PO}_2 \) symmetric stretching band, which shifted towards a lower frequency (1150 cm\(^{-1}\)). This variation may be related to the decondensation of \( \text{Zn}(\text{PO}_3)_2 \) by \( \text{Bi}^{3+} \) ions, which leads to the formation of short chain phosphates.\(^{15}\) The stretching vibration of \( \text{PO}_3 \) groups is an indication of the increasing covalent character of the \( \text{Bi}–\text{O}–\text{P} \) bond. This covalent character is in favor of the glass forming ability of \( \text{Bi}^{3+} \) ions. Several authors\(^{16}\) reported that in the glasses containing bismuth oxide, the glass forming nature of \( \text{Bi}^{3+} \) can be confirmed by the presence of highly distorted \( \text{Bi}_2\text{O}_3 \) polyhedra. The corresponding band in the FT–IR spectra can be observed between 350 and 500 cm\(^{-1}\). In the present systems for \( x = 0 \) (Fig. 5) the appearance of a band in the region, 450–550 cm\(^{-1}\), was assigned to the deformation vibrations of phosphate groups.\(^{16}\) With the addition of \( \text{Bi}_2\text{O}_3 \), these bands were assigned to overlapping vibrations of \( \text{Bi}–\text{O} \) bonds in distorted \( \text{Bi}_2\text{O}_3 \) octahedra with the deformation vibrations of phosphate groups.\(^{16}\) Figure 5 shows that with increasing \( \text{Bi}_2\text{O}_3 \) content, the band shifted towards a higher frequency, which suggests that these bands are associated with the vibrations of \( \text{Bi}–\text{O} \) bonds. Moreover, the increase in frequency of \((\text{P}–\text{O}–\text{P})_{\text{m}} \) groups (from 900 to 915 cm\(^{-1}\)) is in accordance with the presence of pyrophosphate groups\(^{17,18}\) and the frequency of \((\text{PO}_2)_{\text{g}} \), groups are shifting towards a lower wave number. The intensity of the band at 1100 cm\(^{-1}\) did not change when compared to the intensity of \( \nu_{\text{as}} \) of the \( \text{P}–\text{O}–\text{P} \) bridges at 900 cm\(^{-1}\). This was attributed to the \( \nu_{\text{as}} \) of \( \text{PO}_2 \) groups in the short phosphate chains.\(^{19}\) The intensity of the peak at approximately 820 cm\(^{-1}\) decreased with increasing \( \text{Bi}_2\text{O}_3 \) content and the intensity of the peak at approximately 620 cm\(^{-1}\) increased. This might be due to the conversion of \( \text{BO} \) (bridging oxygen atoms) into NBOs.
4. Conclusions
The effect of Bi$_2$O$_3$ addition to Zn(PO$_3$)$_2$ glass was examined in $(50 - 2x)$ZnO–$x$Bi$_2$O$_3$–$(50 + x)$P$_2$O$_5$. The change in molar volume with Bi$_2$O$_3$ content suggests that Bi$_2$O$_3$ depolymerizes the phosphate chains and modifies the structure depending upon the composition. Both the density, VM and $T_g$ increased with increasing Bi$_2$O$_3$ content. The cut-off wavelength in the UV-vis region showed a red shift with increasing Bi$_2$O$_3$ content in the glass systems. The optical band-gap energy decreased with increasing Bi$_2$O$_3$ content. The FTIR spectra showed the rapid depolymerization of phosphate chains with increasing Bi$_2$O$_3$ content, the formation of P–O–Bi bonds and the incorporation of Bi as BiO$_6$ octahedra in the glass matrix. The formation of PO$_3$ groups occurred at higher Bi$_2$O$_3$ concentrations (15 mol%). The existence of the stretching vibration PO$_3$ groups is an indication of the increasing covalent character of the P–O–Bi bond. This covalent character promotes the glass forming ability of Bi$^{3+}$ ions.

Acknowledgement This study was supported by a grant-in-aid for the National Core Research Center Program from the Ministry of Education Science & Technology and the Korea Science & Engineering Foundation (No. R15–2006 – 022– 01001– 0).

References