The effect of bismuth on the structure and mechanical properties of GeO$_2$–PbO–Bi$_2$O$_3$ ternary bulk glass system

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This paper reports the elastic properties and structure of GeO$_2$–PbO–Bi$_2$O$_3$ ternary bulk glasses which were successfully prepared by melt quenching technique. The study was performed by ultrasonic measurements and Fourier transform infra red (FTIR) spectroscopy. Increasing values of density, ultrasonic velocity and elastic moduli were observed due to substitution of bismuth to lead atoms with fixed composition of GeO$_2$. Also, FTIR spectrum showed different profiles between samples with higher content of lead or bismuth. In Pb-rich samples all of the components contributed in the structure as network former; however, in Bi-rich samples lead and bismuth showed modifier behavior and the structure was depolymerized by adding of bismuth content.

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1. Introduction

Lead-germanate glasses show one of the lowest cut-off optical phonon energy among heavy-metal-oxides which results in low nonradiative relaxation rates and hence cause easily observable upconversion. On the other hand, bismuth-germanate glasses are known by high thermal expansion, low transition temperature, excellent infrared transmission, high density, high linear and nonlinear refractive index which make them suitable for non-linear optics and optical switching applications. Moreover, germanate’s well known anomaly and its open questions attract considerable scientific interest. So far researchers have studied germanate glasses containing PbO and Bi$_2$O$_3$ by various techniques such as IR, Raman, XSAFS etc.

Ultrasonic technique is an essential technique to study the elastic properties and structural characteristics of glassy materials. The ultrasonic wave velocities combined with density of glass can be used to determine the elastic properties of glass matrix which are closely associated with the glass structure. On the other hand, IR techniques such as FTIR are powerful techniques to study the vibrational modes in glass network which also significantly related to the glass structure. In order to design a glass for specific application, basic understanding of the glass structure which can influence the macroscopic properties of material is critical.

Hence, the ultrasonic and IR measurements contribute to understand structural characteristics and elastic properties of glass network. Thus, the present study focuses on the relationship between the elastic properties and the structure of GeO$_2$–Bi$_2$O$_3$–PbO ternary glass by means of the ultrasonic pulse-echo and FTIR techniques.

2. Experimental procedure

2.1 Preparation of the glasses

Each glass samples were successfully synthesized by conventional melt-quenching method. Precursors with purity of more than 99% were used to prepare glass (GeO$_2$)$_{0.5}$–(PbO)$_{0.5}$–(4Bi$_2$O$_3$)$_x$ samples with molar concentration of $x = 0, 0.1, 0.2, 0.3, 0.4$, and $0.5$ mol %. Each of glass samples were denoted with GPB50, GPB51, GPB52, GPB53, GPB54 and GPB55 in Table 1. After mixing of GeO$_2$, PbO and Bi$_2$O$_3$ with definite composition and drying the mixture in 300°C, the mixture was melted in furnace at 1100°C for 1 h. Then, the melt was quenched into the preheated metal mould to obtain transparent glass cylinder with 12 mm diameter. The glass samples were then annealed in 420°C for 1 h in order to relieve the mechanical stress. The cylindrical samples were cut and polished with 1–2 centimeter high for ultrasonic measurements and also were made in powder form in a metal plunger for XRD and FTIR measurements.

2.2 Measurements

The prepared glasses were analysed by X’Pert Pro Panalytical PW 3040 MPD X-ray powder diffraction instrument to test their amorphicity. The density of the glasses was determined by Archimedes method as described elsewhere. The MATEC MBS-8000, ultrasonic pulse-echo technique instrument was used to obtain the wave velocities travelled in the glass samples. All measurements were taken at 5 MHz frequency and at room temperature.

Elastic moduli (longitudinal, shear, bulk and Young’s) and Poisson’s ratio of glasses with different contents were determined from the measured ultrasonic velocities and density using the

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Fractal bond connectivity \(d\) is derived from elastic moduli or Poisson’s ratio by relation: \(^{12}\)

\[
d = \frac{4S}{B} = 6 \left( 1 - 2\sigma \right) \frac{1}{1 + \sigma}
\]

FTIR result extracted from the Perkin-Elmer Spectrum-100, FT-IR spectrometer by using of UATR accessory for sampling method. The spectrum were taken from 400 to 1000 cm\(^{-1}\) wavenumbers and deconvoluted into Gaussian component bands.

### 3. Results and discussion

#### 3.1 XRD, density and molar volume

As shown in Fig. 1, no narrow intense peak in the XRD diagram was observed. This shows that the samples are homogeneously amorphous due to no crystalline phase formed. Figures 2(a) and 2(b) show variation of density and molar volume of \((\text{GeO}_2)_{0.5}(\text{PbO})_{0.5-x}(\text{Bi}_2\text{O}_3)_x\) versus bismuth composition respectively. The results can be discussed within two regions: samples with higher amount of lead named Pb-rich (samples GPB550, GPB541 and GPB532, \(0 \leq x \leq 0.2\)) and samples with higher amount of bismuth named Bi-rich samples or region (samples GPB523, GPB514 and GPB505, \(0.3 \leq x \leq 0.5\)). Increase in density in Pb-rich and Bi-rich and decrease in intermediate region is observed due to their higher atomic weight.

Molar volume treats exactly in inverse manner as compared to their density. Decrease in Pb-rich samples, sudden increase between samples GPB532 and GPB523 and decrease in Bi-rich region versus \(x\), can be observed in molar volume diagram. This can indicate the material network contract in Pb and Bi-rich with the increase of Bi content, but a significant difference in network interstices volume between two regions can be distinguished (anomaly). Closer packing in the network can occur by ring size reduction, mean ratio of bending to stretching force constants for the bonds in glass\(^{13}\) or existence of non-direct bands of modifier ions in void space.\(^{14}\)

#### 3.2 Ultrasonic velocities and elastic moduli

Table 1 presents the measured values of ultrasonic longitudinal and shear wave velocities where the longitudinal velocity increases from 3172 to 3476 m/s and the shear one increases from 1776 to 2107 m/s. Both velocities increase however with slightly different slope in two ranges (Table 2). Variations of \(V_L\) and \(V_S\) are dependent on bond strength, packing density, coordination number and cross-linking of units.\(^{14}\) Elastic moduli calculated from density and ultrasound velocities and their

<table>
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<th>Sample code</th>
<th>(x)</th>
<th>(\rho) (g/cm(^3))</th>
<th>(V_{\text{mol}}) (cm(^3))</th>
<th>(V_L) (m/s)</th>
<th>(V_S) (m/s)</th>
<th>(L)</th>
<th>(S)</th>
<th>(B)</th>
<th>(Y)</th>
<th>(l) (nm)</th>
<th>(\sigma)</th>
<th>(d)</th>
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<td>0.458</td>
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![Fig. 1. X-ray diffraction pattern of \((\text{GeO}_2)_{0.5}(\text{PbO})_{0.5-x}(\text{Bi}_2\text{O}_3)_x\) ternary glass.](image1)

![Fig. 2. (a) Density and (b) molar volume of \((\text{GeO}_2)_{0.5}(\text{PbO})_{0.5-x}(\text{Bi}_2\text{O}_3)_x\) glass.](image2)
 increase in the role of Bi and Pb. Higazy et al. mentioned, shear and lattice energy. This mechanism was discussed previously for (Young law was proposed for isostructural compounds which relates bulk and Young moduli, Poisson ratio of (GeO2)0.5(PbO)0.5(Bi2O3)0.5 glass

<table>
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<tr>
<th></th>
<th>ρ (g/cm³)</th>
<th>ρ(Å)</th>
<th>ρ(Å)</th>
<th>L (Å)</th>
<th>S (Å)</th>
<th>B (Å)</th>
<th>Y (Å)</th>
<th>σ (GPa)</th>
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<td>0.76</td>
<td>1.6</td>
<td>945</td>
<td>670</td>
<td>46.8</td>
<td>18.1</td>
<td>22.7</td>
<td>43.6</td>
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<tr>
<td>Intermediate</td>
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<td>2.5</td>
<td>300</td>
<td>370</td>
<td>10.1</td>
<td>8.1</td>
<td>-0.8</td>
<td>17</td>
</tr>
<tr>
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<td>0.67</td>
<td>1.2</td>
<td>425</td>
<td>800</td>
<td>26.5</td>
<td>23.5</td>
<td>-4.8</td>
<td>46.1</td>
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</tbody>
</table>

![Elastic moduli of (GeO2)0.5(PbO)0.5(Bi2O3)0.5 glass.](image)

Table 2. Slope of changes in diagrams of density, molar volume, longitudinal and shear ultrasonic velocities and moduli, bulk and Young’s moduli, Poisson’s ratio of (GeO2)0.5(PbO)0.5(Bi2O3)0.5 glass

![Log(B) vs Log(Vm) according to power law.](image)

![Log(B) vs Log(Vm) according to power law.](image)

Fig. 4. Linear dependence of log(B) to log(Vm) according to power law.

Table 3. First-order stretching force constant (f) calculated from Pauling radii of cations and anions, number of network bond per unit formula (n), number of cross-link per unit cation (n)

<table>
<thead>
<tr>
<th></th>
<th>f(N/m)</th>
<th>n_i</th>
<th>n_i</th>
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<tr>
<td>GeO2</td>
<td>236.5</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>PbO</td>
<td>97.8</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Bi2O3</td>
<td>118.5</td>
<td>3</td>
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</table>

modulus (B) and mean atomic volume (Vm):

\[ B \propto V_m^{m} \]

In silicate glass the values of \( m \) can be adjusted equal to 4/3 or other positive or negative values. Isostructured components with lattice structure and ionicity (i.e. same nature of bonding and co-ordination of polyhedral structural units) can show linear dependence on \( B \) to \( V_m^{4/3} \) which can be adjusted equal to 4/3 or other positive or negative values. This mechanism was discussed previously for the role of Bi and Pb. Higazy et al. mentioned, shear and Young’s moduli have a direct relationship with bond bending (Fb) and bond stretching (Fs) force constant respectively. So, the increase in Y values with Bi2O3 can be attributed to the increase in Fs and the increase of S with Bi concentration can indicate the increase in Fb.

![Elastic moduli of (GeO2)0.5(PbO)0.5(Bi2O3)0.5 glass.](image)

3.3 Power law of bulk modulus and ring deformation model

According to Soga and Ota et al. the so-called 4/3 power law was proposed for isostructural compounds which relates bulk modulus (B) and mean atomic volume (Vm):

\[ B \propto V_m^{4/3} \]

By supposing of \( F_b \) in Nm⁻¹ and \( F \) in nm, bulk modulus will be measured in GPa. Ring size is supposed as the diameter of the atomic rings, i.e. smallest closed circle of A-O bonds. Average bond bending force, \( F_b \), in first approximation may be taken as average bond stretching force (F) which for 3D polycomponent glass is given by:

\[ F = \frac{\sum (x_i f_i)}{\sum (x_i)} \]

\[ f = \frac{1.7}{r^2} \]
where $r$ is the bond length between cation and anion, $f$ is first-order stretching force constant between cation and anion and $n_f$ is the number of network bond per unit formula (Table 3).

Figure 5 shows the dependence of ring size on composition of $(\text{GeO}_2)_{0.5}(\text{PbO})_{0.5}x(\text{Bi}_2\text{O}_3)x$ glass. By increasing of Bi$_2$O$_3$, atomic ring size decreases from 4.72 to 4.56 Å in Pb-rich limit and stays approximately constant in Bi-rich region. It is known that atomic ring size which is a geometrical value decreases by increasing of cross-link density caused by gradual changes in composition. Therefore, apparent decrease of ring size in Pb-rich range by increasing of $x$ indicates significant increase in cross-link density. But, nearly constant values of ring size in intermediate and Bi-rich region indicate that cross-linking density in this region stayed unchanged.

3.4 Poisson’s ratio, fractal bond connectivity

Compositional variation of experimental values of Poisson’s ratio is demonstrated in Fig. 6. Poisson’s ratio decreases in full range but faster in Bi-rich. According to Bridge et al., the cross-link density of two, one and zero are related to Poisson’s ratio of 0.15, 0.3 and 0.4 respectively. Poisson’s ratio starts from 0.27 in Pb-rich and decreases to 0.21 in Bi-rich limit which means the cross-link density increases from nearly one to two.

Fractal bond connectivity can give information about the dimensionality of the glass structure. Namely, values of “d” represent different dimensionalities: $d = 1$ for 1D chain structure, $d = 2$ for 2D layer structure and $d = 3$ for 3D tetrahedral coordination polyhedral. According to Table 1, the fractal bond connectivity for $(\text{GeO}_2)_{0.5}(\text{PbO})_{0.5}x(\text{Bi}_2\text{O}_3)x$ glass increases in full range from 2.15 to 2.88, but high increase in Bi-rich region is seen. In Pb-rich range $d < 2.5$, but in Bi-rich side mainly $d > 2.5$; meaning that the dimensionality in Pb-rich region is predominantly 2D, but by increasing of bismuth content, in Bi-rich region, it tends to be 3D structure.

3.5 FTIR

FTIR absorption spectra of heavy metal oxide germanate glasses are shown in Fig. 7. In this figure envelopes at around 450–500, 500–600 and 700–800 cm$^{-1}$ wavenumbers are recognized. The difference in profile of the spectrum in two ranges of samples (Pb-rich and Bi-rich) is noticeable. Pb-rich samples showed all three envelopes but in Bi-rich limit 700–800 cm$^{-1}$ envelope is stronger and absorption in 450–500 cm$^{-1}$ are not observed; except, sample GPB514 ($x = 0.4$) with very week absorption peak but still strong 700–800 cm$^{-1}$ envelope.

Table 4 contains values of wavenumbers of deconvoluted peaks. The peak at 470 cm$^{-1}$ related to bending vibration of Bi-O bond in strongly distorted BiO$_6$ octahedral units and symmetric bending vibration of Pb-O in PbO$_4$ tetragonal pyramid. Absorption in 550 cm$^{-1}$ is relevant to bending and
symmetric stretching vibration of Ge–O–Ge in GeO$_2$ tetrahedral unit$^{10}$ and also related to antisymmetric bending vibration of Pb–O–Pb,$^9$ and Bi–O$^{(3)}$ vibration bond of BiO$_x$ unit.$^{18}$ High wave-number envelope is deconvoluted to two peaks: one peak in 710 cm$^{-1}$ which is related to stretching vibration of Ge–O–Ge bond in GeO$_2$ octahedral units of rutile GeO$_2$;$^{21}$ and the other peak in 770 cm$^{-1}$ which is related to antisymmetric stretching vibration of Ge–O–Ge bond in tetrahedral units.$^9$

Pyramidal BiO$_3$ unit has a characteristic peak at 830 cm$^{-1}$. Absence of this peak means that only BiO$_x$ units participate in glass structure. The peak in 470 cm$^{-1}$ is related to PbO covalent bond and bending Bi–O bond of BiO$_x$ group which are formed when both Pb and Bi act the role of former in glass matrix. Absence (or weak existence) of this peak in Bi-rich samples, in contrast with Pb-rich region, clearly showed that modification role of both lead and bismuth is predominant in this region which is in good agreement with elastic results. This result is in good accordance with other researches. The low content of bismuth ions in (100–$x$)GeO$_2$-$x$Bi$_2$O$_3$ participate in the glass network, however at high composition they has the role of network modifier.$^{41}$ Lead ions in the germanate-lead oxide system also, act as modifier in low PbO content, but, participate in the glass network in high composition as PbO chains.$^{4,5}$

The envelop at 700–800 cm$^{-1}$ was deconvoluted to two peaks at 710 and 770 cm$^{-1}$ which are related to GeO$_2$ and GeO$_3$ units respectively. This shows the existence of both four and six coordinations. Table 4 shows coordination number ($CN$) derived from formula proposed by Dachille and Roy,$^{22}$ who relates empirically the coordination number of cation $T$ to the wavelength of the strongest infrared peak which is because of the $T$–X stretching bond in $TX_2$ compounds like SiO$_2$, GeO$_2$ and BeF$_2$:

$$K = \frac{CN \cdot \mu(A_1 + A_3)^{1/3}}{ZtZ_XA^1}$$  
(6)

where $\mu$, $A$ and $Z$ are reduced mass, atomic number and valance of atoms $T$ and $X$ which are shown with indices $T$ and $X$ respectively and $K$ is a constant. By assuming of $\mu$ in atomic mass unit and $A$ in $\mu m$, Dachille and Roy proposed the average value of $K$ = 0.168 from experimental results of some $TX_2$ compounds. In this study, the FTIR peak in 853 cm$^{-1}$ extracted from crystalline GeO$_2$ is representative wavenumber when all germanium atoms are 4-fold coordinated.

Substituting of this wavenumber in the Dachille and Roy relation leads to $K = 1.63$ which holds with previous results with slightly different value.$^{23,24}$ Also, the fraction of Ge atoms in 6-fold coordination ($N_6$)$^{24}$ which is evaluated by relation $N_6 = (CN/2) – 2$ from experimental coordination number, is shown in Table 4. According to the recent equations, average coordination number and fraction of Ge atoms in 6-fold coordination were evaluated. Average coordination number decreases from 5.63 to 5.23 and $N_6$ from 0.81 to 0.61 by increasing of bismuth content which show the existence of $CN$ values of both six and four; but 6 predominant specially in Pb-rich limit.

Figure 8 shows gradual decrease of $CN$ in full ranges but with a step-down between Pb-rich and Bi-rich ranges which is related to the gradual change in germanium coordination from 6 to 4 with the sudden coordination change in intermediate region. This may cause an increase in Molar volume especially in intermediate region; although it is compensated in Pb-rich regime by increasing of PbO chains and in Bi-rich region by domination of modification role of contents.

4. Conclusion

In this paper the elastic properties and structure of (GeO$_2$)$_{50}$–(PbO)$_{50–x}$–$x$Bi$_2$O$_3$ ternary bulk glass system, were studied through ultrasonic and FTIR measurements. For this type of glass, both ultrasonic velocities and elastic moduli increased with increasing of bismuth content. The Pb-rich and Bi-rich behaviors are in accordance to the power law. In Pb-rich region with the increase of bismuth content molar volume increased which indicates the opening of the structure. Also, the increase of atomic ring size which related to the decrease of cross-link density was attributed to the presence of longer Pb–O chains in the structure.

FTIR result also showed the existence of covalent Pb–O–Pb in PbO$_x$ and bridging Bi–O–Bi in BiO$_x$ units in this regime. On the other hand, in Bi-rich region, by increasing of bismuth composition, molar volume decreased which indicates the closing of the structure. Approximately, constant ring size related to the almost unchanged cross-link density in this region. Also, disaffiliation of covalent Pb–O–Pb and bridging Bi–O–Bi and participation of just Bi–O$^{(3)}$ and ionic Pb–O in FTIR spectrum confirm the modifier behavior of Bi-rich regime. In addition, existence of both GeO$_2$ and GeO$_3$ units and change of $CN$ from 6 to 4 by increasing of bismuth content (and step-like decrease at intermediate range) may cause an increase in molar volume in intermediate regime but compensate in Bi-rich and Pb-rich regime.

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Table 4. Deconvoluted wavenumbers extracted from FTIR spectrum, coordination number of germanium and fraction of Ge atoms in 6-fold coordination in (GeO$_2$)$_{50}$–(PbO)$_{50–x}$–$x$Bi$_2$O$_3$ ternary glass

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<th>Sample code</th>
<th>$x$</th>
<th>$V_1$</th>
<th>$V_2$</th>
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Fig. 8. Dependence of coordination number of germanium to bismuth composition of (GeO$_2$)$_{50}$–(PbO)$_{50–x}$–$x$Bi$_2$O$_3$ glass.