

# IR and Raman Spectra Properties of Bi<sub>2</sub>O<sub>3</sub>-ZnO-B<sub>2</sub>O<sub>3</sub>-BaO Quaternary Glass System

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## Abstract

Among new low-melting-point glasses, bismuth ate glass is deemed to have the most potential as an environmentally friendly replacement for polluting Pb-containing glasses. Current studies of boro-bismuthate glasses focus on the structural influence of the additional oxide in the context of low-melting-point electronic sealing applications. In this study, the structure of quaternary Bi<sub>2</sub>O<sub>3</sub>-ZnO-B<sub>2</sub>O<sub>3</sub>-BaO glasses was investigated spectroscopically, with Fourier-transform-infrared (FT-IR) and Raman spectra recorded for glasses with different main oxide contents. Signals in the FT-IR are mainly observed around 500 cm<sup>-1</sup>, 720 cm<sup>-1</sup>, 840 cm<sup>-1</sup>, 980 - 1080 cm<sup>-1</sup>, and 1200 - 1500 cm<sup>-1</sup>, while the Raman scattering peaks are located at 130 cm<sup>-1</sup>, 390 cm<sup>-1</sup>, 575 cm<sup>-1</sup>, 920 cm<sup>-1</sup>, and 1250 cm<sup>-1</sup>. The glasses are mainly structured around [BO<sub>3</sub>] units and the numbers of [BiO<sub>6</sub>] and [BiO<sub>3</sub>] units increase with the Bi<sub>2</sub>O<sub>3</sub> content increasing. Concurrently, the FT-IR absorption peaks associated with [BO<sub>4</sub>] units shift to lower wave numbers, indicating a loosening of the glass structure. However, as the B<sub>2</sub>O<sub>3</sub> content is increased, the numbers of [BO<sub>3</sub>] and [BO<sub>4</sub>] units increase, while those of [BiO<sub>3</sub>] and [BiO<sub>6</sub>] units decrease, highlighting a densification of the glass structure. ZnO acts as a network modifier in these glasses.

## Keywords

IR and Raman Spectra, Bi<sub>2</sub>O<sub>3</sub>-ZnO-B<sub>2</sub>O<sub>3</sub>-BaO Quaternary Glass System, Structure

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## 1. Introduction

The special properties of bismuth glass have been investigated mainly in the Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> [1] [2] and Bi<sub>2</sub>O<sub>3</sub>-

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ZnO-B<sub>2</sub>O<sub>3</sub> systems [3]. Greater information is becoming available on its structure and properties [4]-[6]. Bi glass benefits from a low melting point, below 1100°C, and could therefore be developed as a new type of lead-free low-melting-point sealing glass.

Bismuth borate glass has gradually been drawing interest among researchers as a new kind of lead-free material, leading to greater information becoming available on its structure and performance. Raman and infrared (IR) spectroscopy provide important information on the local structure of vitreous and ceramic materials [7] [8]. Shashidhar Bale *et al.* [2] studied the role of Bi<sub>2</sub>O<sub>3</sub> in the formation of the glass network by Raman and IR techniques. Chahine *et al.* [9] reported IR and Raman spectra of sodium-bismuth-copper phosphate glasses, reflecting the structural role of bismuth. Yin *et al.* [1] studied the structure and crystallization kinetics of Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glasses and Radu *et al.* [10] employed IR and Raman spectroscopy to investigate the structural units in bismuth based glasses. Elsewhere, Katerina Knoblochova *et al.* [11] investigated the Bi<sub>2</sub>O<sub>3</sub>-PbO-B<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub> system and analyzed the structure of the glasses.

In this study, the spectroscopic properties of the quaternary Bi<sub>2</sub>O<sub>3</sub>-ZnO-B<sub>2</sub>O<sub>3</sub>-BaO glass system were studied by Fourier transform (FT)-IR and Raman spectroscopy. Variations in the glass structure were investigated on the basis of the spectra to understand the relationship between the atomic-level structure and the bulk properties of the glasses.

## 2. Experimental Procedure

Glass samples of compositions (65 -  $x$ )Bi<sub>2</sub>O<sub>3</sub>- $x$ ZnO-5BaO-30B<sub>2</sub>O<sub>3</sub> ( $3 \leq x \leq 15$  mol%) and (80 -  $y$ )Bi<sub>2</sub>O<sub>3</sub>- $y$ B<sub>2</sub>O<sub>3</sub>-15ZnO-5BaO ( $20 \leq y \leq 40$  mol%) were prepared by melt quenching using reagent grade Bi<sub>2</sub>O<sub>3</sub>, ZnO, and H<sub>3</sub>BO<sub>3</sub>. The precursor chemicals were mixed in porcelain crucibles, calcined at 450°C for 1 h and then melted at 1100°C - 1200°C depending on the glass composition. The melts were stirred for 1 h to homogenize the mixtures. The clear melts (free of bubbles) were quickly cast in stainless steel molds kept at 250°C and pressed with another steel disc maintained at same temperature. The resulting samples were transparent and their color varied from yellow to light brown with increasing bismuth content. The glasses were then annealed at 300°C for about 8 h to remove thermal stress and strain. In the following, the glass samples with  $x = 3, 6, 9, 12,$  and  $15,$  are named A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub>, A<sub>4</sub> and A<sub>5</sub>, respectively. Similarly, the glass samples with  $y = 20, 25, 30, 35,$  and  $40,$  are named B<sub>1</sub>, B<sub>2</sub>, B<sub>3</sub>, B<sub>4</sub>, and B<sub>5</sub>, respectively.

Infrared spectra of the powdered glass samples were recorded at room temperature in the wavelength range 400 - 2000 cm<sup>-1</sup> using a Nicolet-60-SXB FT-IR spectrometer. These measurements were performed on glass powder dispersed in KBr pellets.

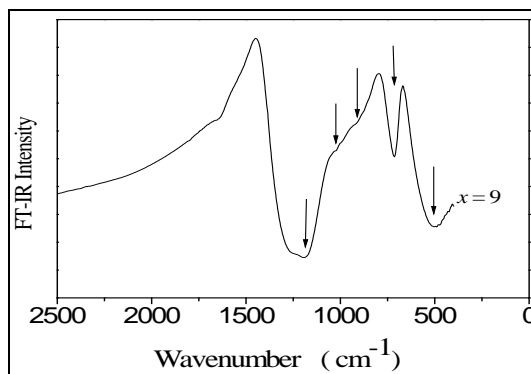
Room-temperature Raman spectroscopy was performed in the 100 - 1700 cm<sup>-1</sup> wavelength range using a Renishaw inVia micro-Raman spectrometer. The incident laser was focused to a diameter of 1 - 2 μm and a notch filter was used to suppress Rayleigh light. Raman shifts were measured to a precision of ~0.3 cm<sup>-1</sup> and the spectral resolution was of the order 1 cm<sup>-1</sup>.

## 3. Results and Discussion

### 3.1. Structure of the Bi<sub>2</sub>O<sub>3</sub>-ZnO-B<sub>2</sub>O<sub>3</sub>-BaO Glasses

**Figure 1** shows the FT-IR spectrum of the  $x = 9$  glass sample, for which absorption bands are clearly observed around 500, 720, 840, 980 - 1080 and 1200 - 1500 cm<sup>-1</sup>. The corresponding assignments are listed in **Table 1**.

FT-IR spectra of glasses are generally interpreted using the method proposed by Tarte [12] and Condrate [13], by comparing the experimental data with those of related crystalline compounds. In this study, the characteristic absorption bands for vitreous Bi<sub>2</sub>O<sub>3</sub> [14] [15] and B<sub>2</sub>O<sub>3</sub> [16] [17] were used. The absorption band centered at ~500 cm<sup>-1</sup> is characteristic of the stretching vibrations of Bi-O bonds in strongly distorted BiO<sub>6</sub> octahedral units [14] [15]. These can overlap with B-O-B bond-bending vibrations [16]-[18]. The absorption band at ~715 cm<sup>-1</sup> has been assigned to the symmetric stretching vibrations of Bi-O bonds in pyramidal BiO<sub>3</sub> units [20], and this can overlap with O<sub>3</sub>B-O-BO<sub>3</sub>-bending vibrations [17] [19]. The absorption band at ~880 cm<sup>-1</sup> arises from symmetric stretching vibrations of Bi-O bonds in pyramidal BiO<sub>3</sub> units [14], possibly superposed with stretching vibrations of B-O bonds in the BO<sub>4</sub> units of diborate groups [17]. The band at ~990 cm<sup>-1</sup> can be attributed to B-Q stretching vibrations in BQ<sub>4</sub> units from tri- (B<sub>3</sub>O<sub>5</sub><sup>-</sup>), tetra- (B<sub>8</sub>O<sub>13</sub><sup>2-</sup>), and penta-borate (B<sub>5</sub>O<sub>8</sub><sup>-</sup>) groups [18]. In the Q<sub>*n*</sub> nomenclature, *n* indicates the number of bridging oxygen for a given network-forming unit, in this case boron. The strong band at ~1200 cm<sup>-1</sup> is assigned to stretching vibrations of B-O bonds in BO<sub>3</sub> units from



**Figure 1.** FT-IR spectrum of a 56Bi<sub>2</sub>O<sub>3</sub>-9ZnO-30B<sub>2</sub>O<sub>3</sub>-5BaO glass.

**Table 1.** Assignments for the FT-IR absorption bands of Bi<sub>2</sub>O<sub>3</sub>-ZnO-B<sub>2</sub>O<sub>3</sub>-BaO glass.

Wavenumber (cm <sup>-1</sup> )	FT-IR assignment
500 cm <sup>-1</sup>	Stretching vibrations of Bi-O bonds in strongly distorted BiO <sub>6</sub> octahedral units, B-O-B bond bending vibrations.
720 cm <sup>-1</sup>	Symmetric stretching vibrations of Bi-O bonds in pyramidal BiO <sub>3</sub> units, O <sub>3</sub> B-O-BO <sub>3</sub> bending vibrations.
840 cm <sup>-1</sup>	Symmetric stretching vibrations of Bi-O bonds in pyramidal BiO <sub>3</sub> units, stretching vibrations of B-O bonds in BO <sub>4</sub> units from diborate groups.
990 - 1080 cm <sup>-1</sup>	Stretching vibrations of B-Q bonds in BQ <sub>4</sub> units from tri-, tetra-, and penta-borate groups.
1200 cm <sup>-1</sup>	Stretching vibrations of B-O bonds in BO <sub>3</sub> units from meta- and ortho-borate groups.
1300 - 1500 cm <sup>-1</sup>	Asymmetric stretching vibrations of B-O bonds in BO <sub>3</sub> and BQ <sub>2</sub> O <sup>-</sup> units.

meta- and ortho-borate groups [19] [21]. The broad shoulder present in the spectrum at ~1295 cm<sup>-1</sup> is assigned to the asymmetrical stretching vibrations of B-O bonds in BO<sub>3</sub> and BQ<sub>2</sub>O<sup>-</sup> units [19] [22].

For all samples, FT-IR absorption bands for vitreous B<sub>2</sub>O<sub>3</sub> were identified at ~720, ~1260, and ~1420 cm<sup>-1</sup>, which are attributed to B-O bond vibrations in trigonal BO<sub>3</sub> units [16]-[18]. The vibrational modes of the borate glass network appear in three infrared spectral regions [19]. The first group of bands, between 1200 and 1600 cm<sup>-1</sup>, arises from the asymmetric stretching relaxation of B-O bonds in BO<sub>3</sub> units. The second group, between 800 and 1200 cm<sup>-1</sup>, is due to B-O bond stretching in tetrahedral BO<sub>4</sub> units, and the third group, around 700 cm<sup>-1</sup>, is due to the bending of B-O-B connections in the borate network [20]. Characteristic absorption bands for crystalline ZnO were identified at ~430 and ~520 cm<sup>-1</sup> and are attributed to Zn-O bond vibrations in tetrahedral ZnO<sub>4</sub> units [23].

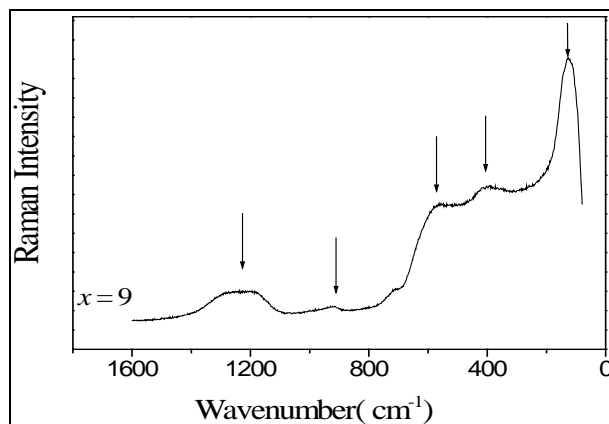
The assignments in **Table 1** suggest that [BiO<sub>6</sub>], [BiO<sub>3</sub>], [BO<sub>3</sub>], and [BO<sub>4</sub>] units may be present in the Bi<sub>2</sub>O<sub>3</sub>-ZnO-B<sub>2</sub>O<sub>3</sub>-BaO quaternary glasses.

Further information on the structure of the glass can be gathered from the absorption peaks around 990 - 1080 cm<sup>-1</sup>, 1200 cm<sup>-1</sup>, and 1300 - 1350 cm<sup>-1</sup>, that are characteristic of [BO<sub>3</sub>] and [BO<sub>4</sub>] units. The FT-IR absorption peaks around 500 cm<sup>-1</sup>, 720 cm<sup>-1</sup>, and 840 cm<sup>-1</sup> can be attributed to the Bi-O bond in [BiO<sub>6</sub>] units and to the B-O bond in [BO<sub>3</sub>] units, or to the Bi-O bond in [BiO<sub>3</sub>] units and the B-O bond in [BO<sub>4</sub>] units. These attributions are however uncertain and can only be confirmed using Raman spectroscopy.

**Figure 2** shows a typical Raman spectrum for these glasses, consisting of broad peaks in the 100 - 1600 cm<sup>-1</sup> range. For the  $x = 9$  glass sample, peaks are observed around 130 cm<sup>-1</sup>, 390 cm<sup>-1</sup>, 575 cm<sup>-1</sup>, 920 cm<sup>-1</sup>, and 1250 cm<sup>-1</sup>.

The vibrational Raman and infrared spectra of the investigated glasses with 45 - 65 mol% bismuth oxide concentrations are dominated by bands associated with structural units built around the heaviest cation, Bi<sup>3+</sup>. The Raman bands arising from heavy metal oxides, such as Bi<sub>2</sub>O<sub>3</sub>, can be classified into four groups: 1) low wavenumber Raman modes (<100 cm<sup>-1</sup>), 2) heavy metal ion vibrations in the range 70 - 160 cm<sup>-1</sup>, 3) bridged anion modes in the intermediate 300 - 600 cm<sup>-1</sup> region, and 4) non-bridging anion modes at higher wavenumbers [24].

The presence of a band around 135 cm<sup>-1</sup> in Raman spectra is evidence for the presence of [BiO<sub>3</sub>] and [BiO<sub>6</sub>]



**Figure 2.** Raman spectrum of a 56Bi<sub>2</sub>O<sub>3</sub>-9ZnO-30B<sub>2</sub>O<sub>3</sub>-5BaO glass.

polyhedra [25]. In the spectrum shown in **Figure 2**, this band is observed at 130 cm<sup>-1</sup>, showing that the Bi<sup>3+</sup> cations are incorporated into [BiO<sub>3</sub>] and [BiO<sub>6</sub>] groups. Considering that the vibrations from bismuth groups appear at significantly lower wavenumbers than those from boron units, the peaks in the 120 - 650 cm<sup>-1</sup> range are assigned to bismuth units with a bridging anion [24] [26]. Thus, the broad and strong band at ~370 cm<sup>-1</sup> in the present Raman spectrum can be attributed to Bi-O-Bi vibrations, while the shoulder at 591 cm<sup>-1</sup> is assigned to Bi-O<sup>-</sup> stretching vibrations in [BiO<sub>6</sub>] octahedral units. Similar observations have been made in lithium bismuthate [27] and other heavy metal oxide glasses [26]. The band around 921 cm<sup>-1</sup> can be ascribed to isolated orthoborate groups [29] while the weak band from 1285 to 1309 cm<sup>-1</sup>, observed over the entire composition range, is due to Bi-O<sup>-</sup> non-bridging oxygens (NBOs) in BiO<sub>3</sub> and pyroborate groups. Indeed, in the infrared spectra from these glasses, the band observed at 708 cm<sup>-1</sup> is assigned to B-O-B bending vibrations in trigonal [BO<sub>3</sub>] groups [21], the band around 1218 cm<sup>-1</sup> arises from Bi-O<sup>-</sup> NBO stretching vibrations of [BiO<sub>3</sub>] units, and the band at 1256 cm<sup>-1</sup> is due to B-O<sup>-</sup> vibrations. To facilitate the interpretation of the spectra, the different Raman peaks and their related functional groups are summarized in **Table 2**.

**Figure 2** and **Table 2** show that [BO<sub>3</sub>], [BiO<sub>6</sub>] and [BiO<sub>3</sub>] units may be present in these boro-bismuthate glasses, but the characteristic peak for [ZnO<sub>4</sub>] units around 254 cm<sup>-1</sup> is not clearly visible in **Figure 2**, suggesting that ZnO acts as a network modifier in this glass system.

Based on the FT-IR and Raman spectra obtained for this glass, the main network forming units are trigonal [BiO<sub>3</sub>] and [BO<sub>3</sub>] groups with a smaller number of [BO<sub>4</sub>] tetrahedrons. However, [BiO<sub>6</sub>] units are not incorporated in the glass network. Bi-O<sup>-</sup> NBOs may be present as well as some Bi-O-Bi and bonds between [BiO<sub>3</sub>] and [BiO<sub>3</sub>] or between [BiO<sub>3</sub>] and [BiO<sub>6</sub>] groups. The connections between [BO<sub>3</sub>] groups, and between [BO<sub>3</sub>] and [BO<sub>4</sub>] groups, may occur via B-O-B bonds or B-O<sup>-</sup> links. ZnO acts as a network modifier and is not integrated in the glass network.

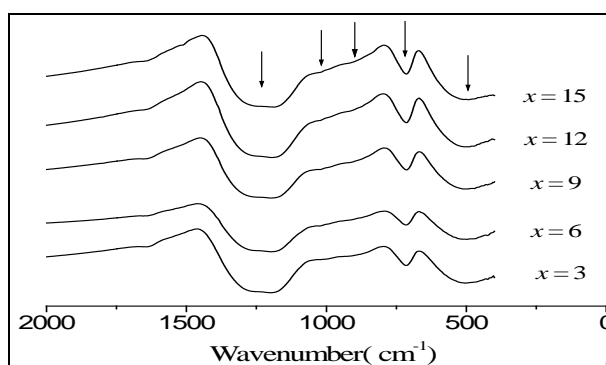
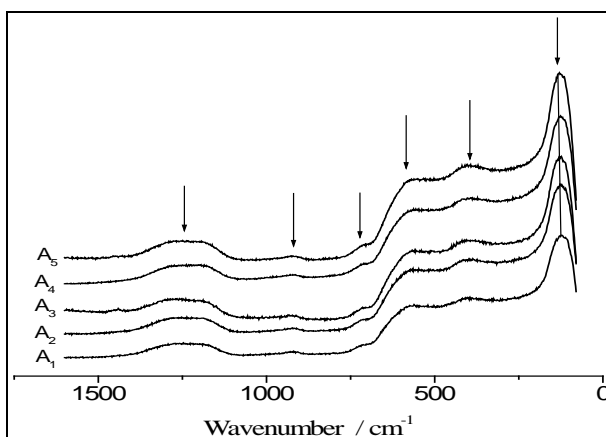
### 3.2. Effect of Bi<sub>2</sub>O<sub>3</sub> Contents on the Structure of Bi<sub>2</sub>O<sub>3</sub>-ZnO-B<sub>2</sub>O<sub>3</sub>-BaO Glasses

Bi<sub>2</sub>O<sub>3</sub> plays a unique role in the structure of these glasses. The presence in large proportions of the two network formers, Bi<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub>, leads to the formation of a vitreous structure with exceptional properties. **Figure 3** shows the FT-IR spectra obtained for glasses in this system with different Bi<sub>2</sub>O<sub>3</sub> contents, with the corresponding Raman spectra shown in **Figure 4**. Both the FT-IR and Raman curves shift slightly with increasing Bi<sub>2</sub>O<sub>3</sub> contents.

The IR absorption spectra obtained from glasses in the Bi<sub>2</sub>O<sub>3</sub>-ZnO-B<sub>2</sub>O<sub>3</sub>-BaO system with different Bi<sub>2</sub>O<sub>3</sub> contents are shown in **Figure 3**. The peak around 500 cm<sup>-1</sup> clearly increases in intensity with increasing Bi<sub>2</sub>O<sub>3</sub> content, indicating an increase in the number of [BiO<sub>6</sub>] units. The peak around 720 cm<sup>-1</sup> also tends to increase in intensity, possibly due to increasing numbers of [BO<sub>3</sub>] and [BiO<sub>3</sub>] units. Similarly, the strengthening of the peak around 990 - 1080 cm<sup>-1</sup> does not change significantly in intensity, it shifts towards lower wave numbers, highlighting the tendency of [BO<sub>4</sub>] units to become looser in the glass structure. Finally, the increase in intensity of the peaks around 1200 cm<sup>-1</sup> and 1300 - 1350 cm<sup>-1</sup> is ascribed to increasing numbers of [BO<sub>3</sub>] units in the glasses.

**Table 2.** Assignments for the Raman scattering bands measured in  $\text{Bi}_2\text{O}_3\text{-ZnO-B}_2\text{O}_3\text{-BaO}$  glasses [3] [4] [29] [30].

Wave number ( $\text{cm}^{-1}$ )	Raman assignment
$130 \text{ cm}^{-1}$	Symmetric stretching vibrations of Bi-O-Bi bonds in pyramidal $\text{BiO}_3$ units and $\text{BiO}_6$ octahedrons.
$254 \text{ cm}^{-1}$	Bending vibrations of Zn-O bonds in $\text{ZnO}_4$ tetrahedrons.
$390 \text{ cm}^{-1}$	Symmetric stretching vibrations of Bi-O-Bi bonds in pyramidal $\text{BiO}_3$ units and $\text{BiO}_6$ octahedrons.
$575 \text{ cm}^{-1}$	Stretching vibrations of $\text{Bi-O}^-$ bonds in $\text{BiO}_6$ octahedrons.
$920 \text{ cm}^{-1}$	Stretching vibrations of B-O bonds in orthoborate formed by pyramidal $\text{BO}_3$ units, stretching vibrations of $\text{Bi-O}^-$ bonds in $\text{BiO}_6$ octahedrons.
$1250 - 1320 \text{ cm}^{-1}$	Stretching vibrations of $\text{Bi-O}^-$ bonds in pyramidal $\text{BiO}_3$ units.
$1250 - 1500 \text{ cm}^{-1}$	Stretching vibrations of $\text{B-O}^-$ bonds and stretching vibrations of $\text{O}_3\text{B-O-BO}_3$ bonds in $\text{BO}_3$ pyramidal units, stretching vibrations of B-O-B bonds in pyramidal $\text{BO}_3$ units.

**Figure 3.** FT-IR spectra of  $(65-x)\text{Bi}_2\text{O}_3\text{-}x\text{ZnO-}5\text{BaO-}30\text{B}_2\text{O}_3$  ( $3 \leq x \leq 15$  mol%) glasses.**Figure 4.** Raman spectra of  $(65-x)\text{Bi}_2\text{O}_3\text{-}x\text{ZnO-}5\text{BaO-}30\text{B}_2\text{O}_3$  ( $3 \leq x \leq 15$  mol%) glasses.

**Figure 4** shows the Raman spectra obtained for glasses with different  $\text{Bi}_2\text{O}_3$  contents. A clear increase in intensity is observed around  $130 \text{ cm}^{-1}$ , which indicates increasing numbers of  $[\text{BiO}_3]$  and  $[\text{BiO}_6]$  units in the glass. Furthermore, from sample  $A_1$  to  $A_5$ , the peaks shift to higher wavenumbers, from  $124 \text{ cm}^{-1}$  to  $136 \text{ cm}^{-1}$ , highlighting an increasing proportion of  $[\text{BiO}_3]$  units. In these glasses, the network is formed around  $[\text{BO}_4]$  tetrahedrons and trigonal  $[\text{BO}_3]$  and  $[\text{BiO}_3]$  units but does not involve  $[\text{BiO}_6]$  units. Bi-O-Bi bonds might be formed between  $[\text{BiO}_3]$  units, or between  $[\text{BiO}_3]$  and  $[\text{BiO}_6]$  units; however, the vibration frequency of Bi-O-Bi bonds varies little between different structural units, since the vibration is stronger inside the network than outside.

The scattering peak around  $390\text{ cm}^{-1}$  in the Raman spectra increases in intensity with increasing  $\text{Bi}_2\text{O}_3$  contents, indicating that the numbers of  $[\text{BiO}_3]$  and  $[\text{BiO}_6]$  units increase in the glass. The peak around  $575\text{ cm}^{-1}$  also becomes stronger, highlighting an increase in the number of  $[\text{BiO}_6]$  units. Finally, the increased intensity of the peak around  $1250\text{ cm}^{-1}$  may be ascribed to greater numbers of  $[\text{BiO}_3]$  and  $[\text{BO}_3]$  units.

To summarize, the FT-IR and Raman spectra of these glasses suggest that bismuth is present in the form of  $[\text{BiO}_6]$  and  $[\text{BiO}_3]$  units, and boron as  $[\text{BO}_3]$  and  $[\text{BO}_4]$  units. ZnO is not incorporated in the network and provides free oxygen atoms. In the glasses with higher  $\text{Bi}_2\text{O}_3$  contents, a clear increase in the numbers of  $[\text{BiO}_6]$  and  $[\text{BiO}_3]$  units is evidenced. The FT-IR absorption peaks at  $990 - 1080\text{ cm}^{-1}$  shift to lower wavenumbers from samples  $\text{A}_1$  to  $\text{A}_5$ , indicating that the  $[\text{BO}_4]$  units tend to become loose in the glass network, the latter being built mainly around trigonal  $[\text{BO}_3]$  groups.

### 3.3. Effect of $\text{B}_2\text{O}_3$ Contents on the Structure of $\text{Bi}_2\text{O}_3$ -ZnO- $\text{B}_2\text{O}_3$ -BaO Glasses

Figure 5 shows the infrared spectra obtained for the glasses in group B. For all compositions, bands around  $500\text{ cm}^{-1}$ ,  $720\text{ cm}^{-1}$ ,  $840\text{ cm}^{-1}$ ,  $980 - 1080\text{ cm}^{-1}$ , and  $1200 - 1500\text{ cm}^{-1}$  are observed. The assignments are similar to those described for group A, showing that the same four structural units— $[\text{BiO}_3]$ ,  $[\text{BiO}_6]$ ,  $[\text{BO}_3]$ , and  $[\text{BO}_4]$ —are present in these glasses.

The absorption band at  $980 - 1080\text{ cm}^{-1}$ , attributed to stretching vibration in  $[\text{BO}_4]$  groups, increases in intensity from sample  $\text{B}_1$  to  $\text{B}_5$ . Higher  $\text{B}_2\text{O}_3$  contents result in stronger B-O-B bond vibrations from trigonal  $[\text{BO}_3]$  units, which appear around  $1100 - 1400\text{ cm}^{-1}$  in the FT-IR spectra. A similar increase is observed for the absorption peak at  $720\text{ cm}^{-1}$ , arising from B-O-B bond stretching vibrations in trigonal  $[\text{BO}_3]$  groups and from symmetric Bi-O stretching vibrations in trigonal  $[\text{BiO}_3]$  units, indicating an increase in the number of these two groups. In contrast, the absorption peak at  $470\text{ cm}^{-1}$ , arising from Bi-O bond bending in  $[\text{BiO}_6]$  octahedrons, weakens.

Figure 6 shows the Raman spectra obtained for different glasses in group B, covering the spectral range of  $100 - 1600\text{ cm}^{-1}$ . For the  $\text{B}_1$  sample, scattering bands are clearly observed at  $130\text{ cm}^{-1}$ ,  $390\text{ cm}^{-1}$ ,  $575\text{ cm}^{-1}$ ,  $920\text{ cm}^{-1}$ , and  $1250 - 1500\text{ cm}^{-1}$ .

As they belong to the same glass system, the samples from groups A and B produce similar Raman peaks, as evidenced by comparing Figure 4 and Figure 6. However, as the  $\text{B}_2\text{O}_3$  content increases, the scattering intensity at  $130\text{ cm}^{-1}$  in the Raman spectra, arising from symmetric Bi-O-Bi stretching vibrations in trigonal  $[\text{BiO}_3]$  groups and  $[\text{BiO}_6]$  octahedron, decreases, highlighting a corresponding decrease in the relative numbers of  $[\text{BiO}_3]$  and  $[\text{BiO}_6]$  units.

As the  $\text{B}_2\text{O}_3$  content increases from sample  $\text{B}_1$  to  $\text{B}_5$ , the band around  $390\text{ cm}^{-1}$ , due to symmetric Bi-O-Bi stretching vibrations in trigonal  $[\text{BiO}_3]$  units and  $[\text{BiO}_6]$  octahedrons, becomes stronger, reflecting enhanced crosslinking of the  $[\text{BiO}_3]$  and  $[\text{BiO}_6]$  groups in the glass network. The peak around  $575\text{ cm}^{-1}$ , associated with Bi-O bond stretching vibrations in  $[\text{BiO}_6]$  octahedrons, decreases in intensity with increasing  $\text{B}_2\text{O}_3$  contents, indicating a decrease in the relative number of  $[\text{BiO}_6]$  units. However, no clear variation is observed for the Raman scattering peak at  $920\text{ cm}^{-1}$ , attributed to B-O bond stretching vibrations in the orthoborate formed by  $\text{BO}_3$  pyramidal units. For all compositions, the Raman scattering peak at  $1250 - 1500\text{ cm}^{-1}$  arises mainly from the

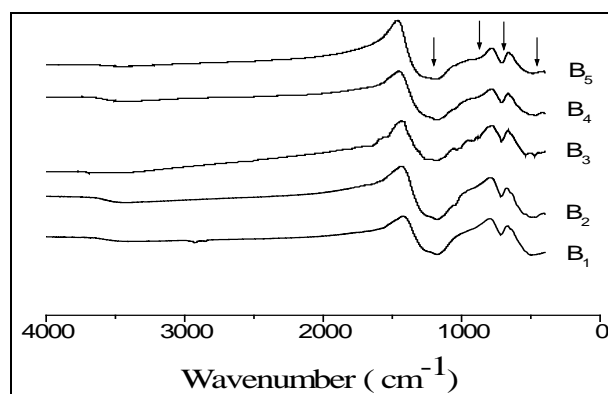
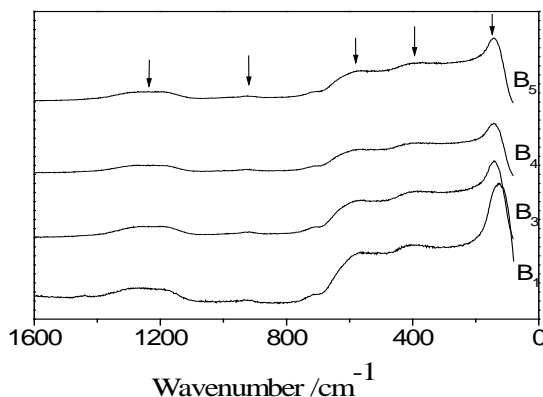


Figure 5. FT-IR spectra of  $(80 - y)\text{Bi}_2\text{O}_3$ - $y\text{B}_2\text{O}_3$ - $15\text{ZnO}$ - $5\text{BaO}$  ( $20 \leq y \leq 40\text{ mol}\%$ ) glasses.





**Figure 6.** Raman spectra of  $(80 - y)\text{Bi}_2\text{O}_3\text{-}y\text{B}_2\text{O}_3\text{-}15\text{ZnO-}5\text{BaO}$  ( $20 \leq y \leq 40$  mol%) glasses.

Bi-O<sup>-</sup> NBO of  $[\text{BiO}_3]$  units and the B-O-B stretching vibration of  $[\text{BO}_3]$  units. As the  $\text{B}_2\text{O}_3$  content is increased in going from sample  $\text{B}_1$  to  $\text{B}_5$ , this peak weakens, indicating a relative decrease and increase in the number of  $[\text{BiO}_3]$  and  $[\text{BO}_3]$  units, respectively. Indeed, the decrease in the Raman peak around  $1250 - 1500 \text{ cm}^{-1}$  suggests that the decrease in the number of  $[\text{BiO}_3]$  units is more substantial than the increase in the number of  $[\text{BO}_3]$  groups.

The above analysis of the B samples suggests that  $[\text{BiO}_6]$ ,  $[\text{BiO}_3]$ ,  $[\text{BO}_3]$ , and  $[\text{BO}_4]$  units are present in the glasses. With increasing  $\text{B}_2\text{O}_3$  content, the relative numbers of  $[\text{BO}_3]$  and  $[\text{BO}_4]$  units increase with a corresponding decrease in the number of  $[\text{BiO}_3]$  and  $[\text{BiO}_6]$  units. It is notable however that no Raman peak assignable to  $[\text{ZnO}_4]$  tetrahedrons appears in the group B glasses.

#### 4. Conclusions

In summary, glasses in the  $\text{Bi}_2\text{O}_3\text{-ZnO-B}_2\text{O}_3\text{-BaO}$  system were prepared and investigated by FT-IR and Raman spectroscopy in terms of the structure of the glass matrix. The FT-IR data suggest that the glass network is built around trigonal  $[\text{BO}_3]$  units, cross-linked or connected to  $[\text{BO}_4]$  groups, while the Raman data highlight the presence of  $[\text{BiO}_3]$  and  $[\text{BiO}_6]$  units. The main network forming species are trigonal  $[\text{BiO}_3]$  and  $[\text{BO}_3]$  units, but  $[\text{BO}_4]$  tetrahedrons form part of the network. The  $[\text{BiO}_6]$  units do not enter the glass network.

When altering the content of the main oxide, only slight changes are observed in the FT-IR and Raman spectra. As the  $\text{Bi}_2\text{O}_3$  content is increased, the absorption and scattering peaks associated with  $\text{Bi}^{3+}$  and  $\text{B}^{3+}$  increase and decrease, respectively. Contrarily, for increasing  $\text{B}_2\text{O}_3$  contents, the peaks arising from  $[\text{BiO}_3]$  and  $[\text{BiO}_6]$  units decrease in intensity, while those from  $[\text{BO}_3]$  and  $[\text{BO}_4]$  units strengthen.

All the results point to the fact that introducing  $\text{Bi}_2\text{O}_3$  leads to a somewhat looser structure, and this is therefore propitious for lowering the melting point of the glass. On the contrary, increasing the  $\text{B}_2\text{O}_3$  content leads to a more compact structure and thus to a more stable glass system.

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