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Effect of Bi_2O_3 on structure and wetting studies of Bi_2O_3–ZnO–B_2O_3 glasses

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ABSTRACT

Glasses with different Bi_2O_3 contents (37–42 mol%) have been prepared by conventional melt quench technique. The IR and Raman studies indicate that these glasses are made up of [BiO_6], [BiO_3], [BO_3] and [BO_4] basic structural units. The vibrations of [BiO_3] and [BO_3] become stronger as the content of Bi_2O_3 increases, which makes glass structure loosened. Viscosity of the glasses was measured by using a Rheotronic III paralleled plate rheometry, which shows that the viscosity of glass samples decreased when the content of Bi_2O_3 increased at the same temperature (400–460 °C). The temperature range which suits for glasses sealing was calculated by using the approximation of Arrhenian behaviour. The wetting performance of Bi_2O_3–ZnO–B_2O_3 glasses was described by using high-temperature microscope, which also proves that the structure of investigated Bi_2O_3–ZnO–B_2O_3 glasses become loosened due to the increasing of the content of Bi_2O_3.

1. Introduction

Lead oxide glass systems have become a kind of popular low temperature sealing glasses for commercial use because of their high structural stability, low glass transitional temperature and good thermal and electrical characteristics [1,2]. Which also have wide applications in the field of glass ceramic, electronic devices, thermal and mechanical sensors, etc. [3–5]. However, lead oxide glass systems should be replaced by lead-free glasses on account of its toxicity to the environment and the human body. Therefore, newly low melting glasses without lead are being evaluated and lead-free glasses are under developing in many research groups [4].

Glasses based on Bi_2O_3–ZnO–B_2O_3 system are expected to be a new kind of sealing glasses because of their low melting temperature. Despite the fact that Bi_2O_3 is not a classical glass former, in the presence of conventional glass formers (such as B_2O_3, SiO_2, etc.) it may build a glass network of [BiO_n] (n = 3 and 6) pyramids [6]. Bi_2O_3 could be a suitable substitute of PbO in the preparation of lead-free glass compositions [7–9].

Infrared and Raman spectroscopy provides important information regarding the local structure in glass and ceramic materials [8,10]. Recently, Shashidher et al. [8] studied the role of the content of Bi_2O_3 on structure in Bi_2O_3–ZnO–B_2O_3 glasses. Radu et al. [11] employed infrared and Raman spectroscopy studies to investigate the structural units in bismuth based glasses. He et al. [12] investigated structure and sintering in Bi_2O_3–ZnO–B_2O_3 glasses. It is well known that the wetting performance of low-melting glass is ruled by the viscous flow and surface tension of the glasses. Therefore, viscosity is one of the most important factors that can determine the melt behaviour of glasses.

In this study, the structure of Bi_2O_3–ZnO–B_2O_3 glasses was studied as a function of Bi_2O_3 content. The viscosity and wetting performance of Bi_2O_3–ZnO–B_2O_3 glasses as a function of Bi_2O_3 content were investigated.

2. Experimental

2.1. Preparation of glass sample

Besides Bi_2O_3, the glass composition contained oxides such as B_2O_3: 39 mol%, ZnO: 42 mol%, BaO: 19 mol%. These oxides kept the same ratio and Bi_2O_3 was introduced into the glass. The glass samples were labeled as A_1, A_2, A_3, A_4 and A_5 for 37, 38, 39, 41 and 42 mol% of Bi_2O_3, respectively.

The basic glass materials were weighed, mixed and placed into corundum crucibles. The corundum crucibles were put into an electric furnace and heated at a rate of about 5 °C/min until the melting temperature was reached (about 1200 °C). The samples were held at the melting temperature for 2 h, and then the melting glass was poured into a preheated stainless die. The glasses were annealed at 320 °C for 0.5 h to eliminate internal stress.

2.2. IR and Raman spectra

Infrared spectra of the powdered glass samples were recorded at room temperature in the range 400–2000 cm^{-1} using a spectrometer (Nexus FT-IR, Thermo Nicolet, USA). These measurements were made on glass powder dispersed in KBr pellets.

The room temperature Raman measurements were performed in the range 100–1600 cm^{-1} using a micro Raman system from Renishow (Invia) spectrometer. The incident laser power was focused on a diameter of 1–2 μm and a notch filter was used to suppress Rayleigh light. In the present system Raman shifts

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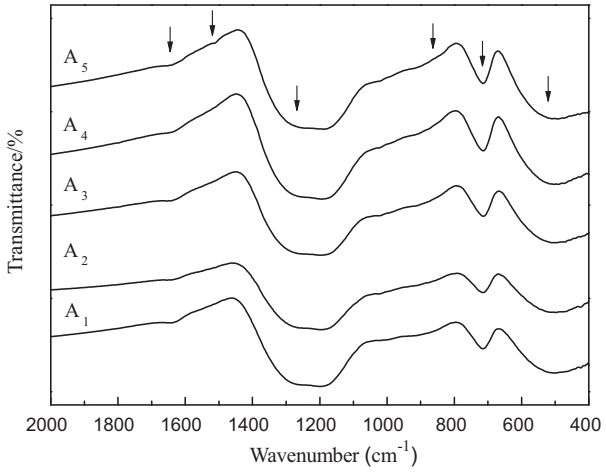

Fig. 1. Infrared spectra of Bi_2O_3–ZnO–B_2O_3 glass system.

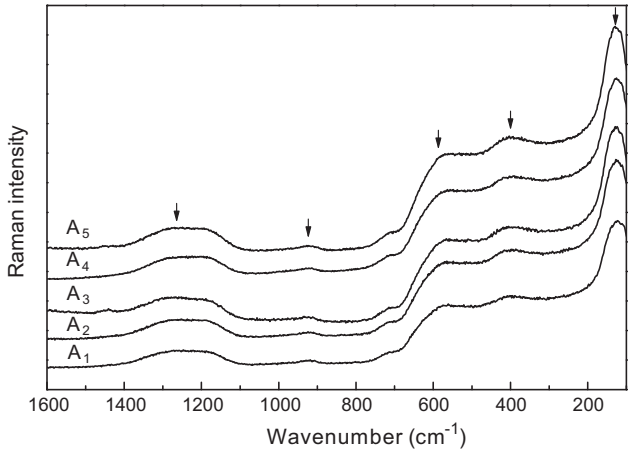

Fig. 2. Raman spectra of Bi_2O_3–ZnO–B_2O_3 glass system.

are measured with a precision of ~0.2 cm^{-1} and the spectral resolution is of the order 1–2 cm^{-1}.

2.3. Thermo-rheological properties characterization

Viscosity of the glasses was measured by using a Rheotronic III paralleled plate rheometry produced by USA THETA, an instrument which can operate up to 1000 °C and has a high temperature sensitivity of 1 °C. The cylinder glass sample has a size of about 8 mm in diameter and 6 mm in height. The paralleled plates used are of a high grade heat-resistant platinum.

The measurement was performed firstly by holding the cylinder glass samples, sandwiched between the paralleled plates and under a fixed force, then the sample compression as a function of time (or temperature) is recorded by raising the temperature at a rate of 6 °C/min under 40 g load applied through the Quartz glass tube. Finally, the viscosity is calculated through the following equation [13,14]:

$$\eta = \frac{2\pi M g h^5(t)}{3V[\mathrm{d}h(t)/\mathrm{d}t][2\pi h^3(t) + V]} \quad (1)$$

where η is the viscosity (Pa s), M is the total applied load to the glass beam (g), g is the acceleration of gravity (980 cm/s^2), $h(t)$ is the sample height at the time t(s) in cm, $\mathrm{d}h(t)/\mathrm{d}t$ is the compression rate at the time t in cm/s and V is the sample volume in cm^3.

2.4. High-temperature microscope analysis

A high-temperature microscope (HTM Reetz GmbH) was used in the experimental work. The glass samples were ground and sieved with a 200 mesh sieve (<75 μm), then the power was compressed to cylinder samples (about diameter 5 mm and height 2.5 mm) by using a hand press. A 439L stainless steel plate (15 mm × 15 mm × 1 mm) was used as the substrate. The measurements were taken in argon gas at a heating rate of 5 °C/min, and a computerized image analysis system recorded the sample geometry during heating. The wetting process between cylinder samples and stainless steel was measured, and the shrinkage, the expansion, the sintering and the softening behaviour of cylinder samples could be observed at elevated temperatures.

3. Results

3.1. IR spectra

Fig. 1 illustrates the infrared spectra of the present glass system. All the glass compositions show bands at ~520 cm^{-1}, ~710 cm^{-1}, ~860 cm^{-1}, ~1270 cm^{-1}, ~1520 cm^{-1}, and 1650–1690 cm^{-1}.

3.2. Raman spectra

Fig. 2 shows the Raman spectra of present glass system in the spectral range 100–1600 cm^{-1} consisting of broad peaks and shoulders.

In the Raman spectra, all the glass compositions show strong band at ~130 cm^{-1}. As the content of Bi_2O_3 increases the band becomes stronger. The strong bands at ~394 cm^{-1} and ~586 cm^{-1} grow in intensity with the increase of content of Bi_2O_3. For all compositions the weak band at ~927 cm^{-1} grows in intensity and shift towards lower wave numbers with the increasing of the content

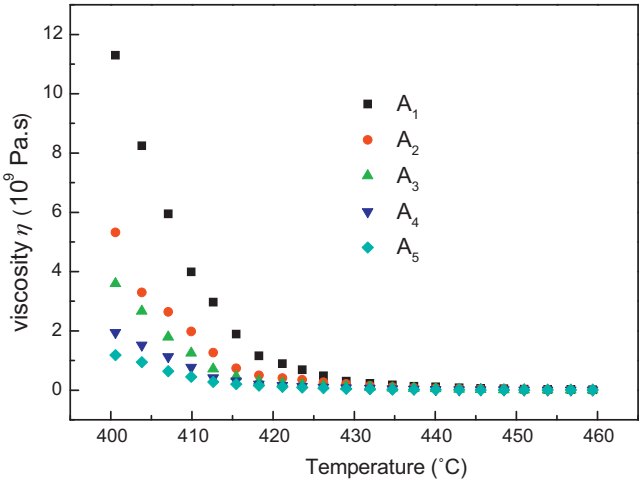

Fig. 3. Viscosity as a function of temperature for Bi_2O_3–ZnO–B_2O_3 glasses.

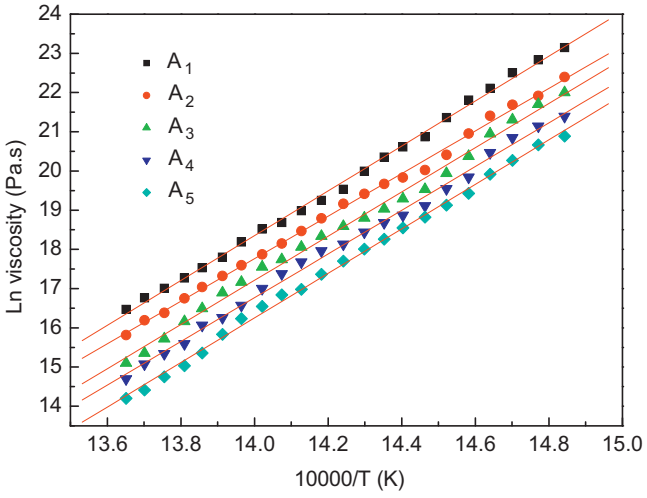

Fig. 4. Ln viscosity vs. 10,000/T for Bi_2O_3–ZnO–B_2O_3 glasses.

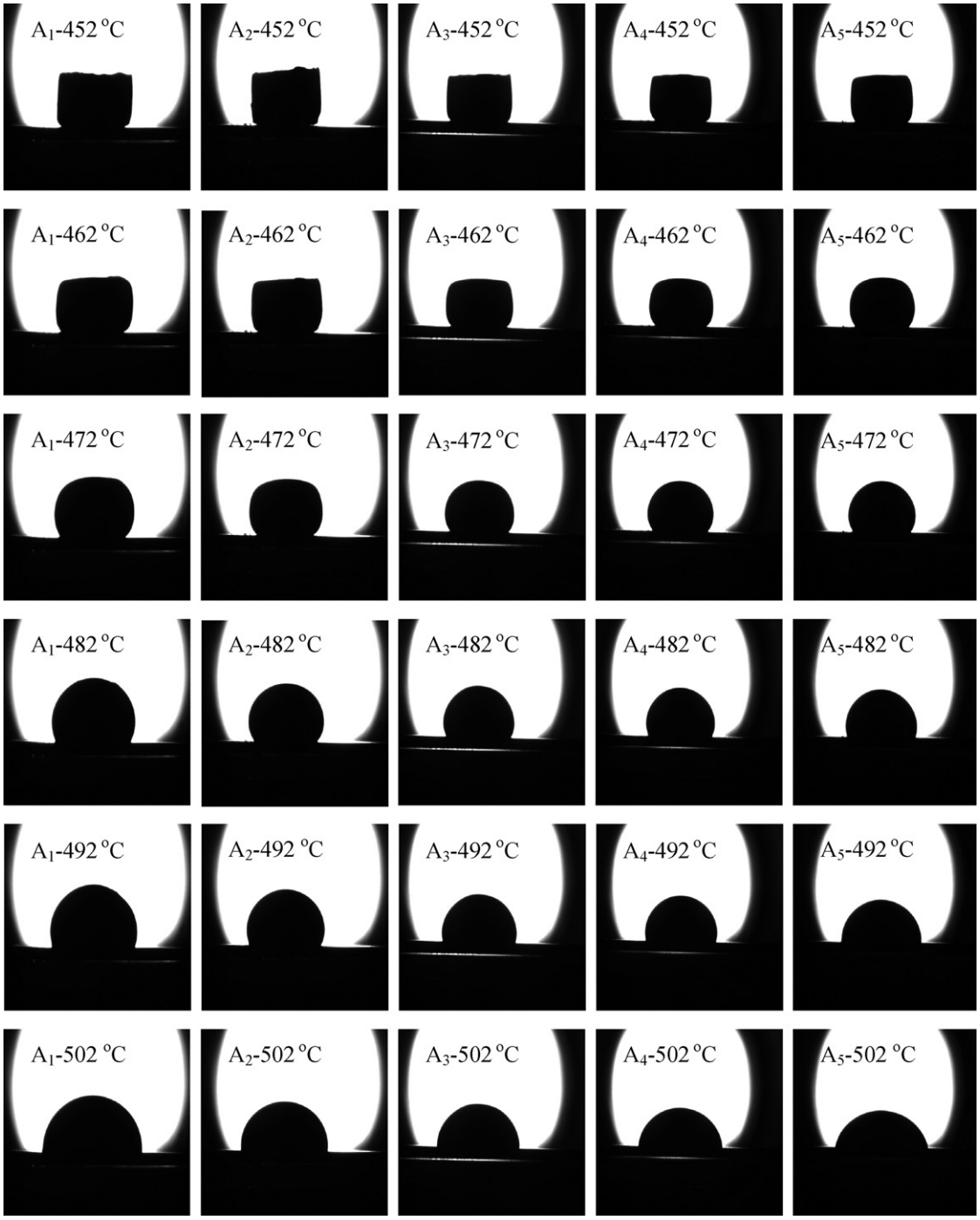

Fig. 5. Shape changes of the A_1, A_2, A_3, A_4 and A_5 samples as a function of temperature (heating rate of 5 °C/min).

of Bi_2O_3. With the Bi_2O_3 increasing, the band at 1258–1278 cm^{-1} becomes stronger.

3.3. Viscosity

Fig. 3 shows the relation between T (°C) and η (Pa s), and the relation between 10,000/T (K) and ln η (Pa s) of Bi_2O_3–ZnO–B_2O_3 glasses could be observed in Fig. 4. The symbols represent the experimental data measured by the paralleled plate method.

It is clear in Fig. 3 that the viscosity of Bi_2O_3–ZnO–B_2O_3 glass decreases as the temperature (400–460 °C) increases. And increasing of Bi_2O_3 in A_1–A_5 at the same temperature between 400 °C and 460 °C leads to the decreasing of the viscosity. Fig. 4 shows nearly linear trends.

3.4. High-temperature microscope

High-temperature microscope was used to record the sample geometry of A_1, A_2, A_3, A_4 and A_5 during heating. It is clear that the morphology of cylinder samples changed as the temperature improves. The shape changes of the cylinder samples occurs due to the viscosity change of the glasses, Fig. 5 shows selected images derived from the high-temperature microscope test. The selection criterion of the images is temperature, which is correspondent with the viscosity.

Table 1
Band position and corresponding assignments of IR spectra of all glass composition.

Bands	Assignment
~520 cm^{-1}	ν_4 vibration of [BO_4] tetrahedra
~710 cm^{-1}	B–O–B bending vibrations in [BO_3] triangles
~860 cm^{-1}	The total symmetrical stretching vibrations of the [BiO_3] and [BiO_6] polyhedra
~1270 cm^{-1}	Bi–O$^-$ stretching vibrations of [BiO_3] triangles
~1520 cm^{-1}	Asymmetrical stretching of [BiO_3] triangles
1650–1690 cm^{-1}	OH bending mode of vibration

Table 2
Band position and corresponding assignments of Raman spectra of all glass composition.

Bands	Assignment
~130 cm^{-1}	Existence of [BiO_3] and [BiO_6] polyhedra
~394 cm^{-1}	Bi–O–Bi vibrations of both [BiO_3] and [BiO_6] octahedral units
~586 cm^{-1}	Bi–O$^-$ stretching vibrations in distorted linked [BiO_6]
~927 cm^{-1}	Isolated orthoborate group
1258–1278 cm^{-1}	Bi–O$^-$ stretching vibrations of [BiO_3] triangles

4. Discussion

4.1. IR, Raman spectra and glass structure

The boron–oxygen network can be in the form of planar [BO_3] and/or tetrahedral [BO_4]. In the IR spectra, the planar [BO_3] gives four fundamental bands around 950 (ν_1), 750 (ν_2), 1250 (ν_3) and 600 (ν_4) cm^{-1}. Tetrahedral [BO_4] unit also gives four bands around 1000 (ν_1), 900 (ν_2), 600 (ν_3) and 550 (ν_4) cm^{-1} [15].

In the IR spectra, the weak band observed at 1650–1690 cm^{-1} is due to OH bending mode of vibration [16]. The weak band at ~520 cm^{-1} is due to ν_4 vibration of [BO_4] tetrahedral [15], it becomes weaker as the content of Bi_2O_3 increases. This result indicates that [BO_4] tetrahedral content in the glass is poor and it decreases as the content of Bi_2O_3 increases. The band at ~710 cm^{-1} is due to B–O–B bending vibrations in [BO_3] triangles [17–19], it becomes more intense with increasing of the content of Bi_2O_3. The band at ~860 cm^{-1} was assigned to the total symmetric stretching vibrations of [BiO_3] and [BiO_6] polyhedra, respectively [20,21]. The band at ~1270 cm^{-1} is due to Bi–O$^-$ stretching vibrations of [BiO_3] triangles [9,16,18], and the band at ~1520 cm^{-1} is due to asymmetrical stretching of [BiO_3] triangles [18]. These bands are all about the vibrations of [BiO_3] triangles, and they all become more intense with increase of the content of Bi_2O_3. The band positions and the corresponding assignments of IR spectra are given in Table 1 for all the glass compositions.

In the Raman spectra, the band at ~130 cm^{-1} shows the existence of [BiO_3] and [BiO_6] polyhedra [22]. It becomes stronger as the content of Bi_2O_3 increases. The band at ~394 cm^{-1} can be attributed to Bi–O–Bi vibrations of both [BiO_3] and [BiO_6] octahedral units [8]. The band at ~586 cm^{-1} can be attributed to Bi–O$^-$ stretching vibrations in distorted linked [BiO_6] [8]. The band at ~927 cm^{-1} can be attributed to isolated orthoborate group [23] while the weak band at 1258–1278 cm^{-1} is due to Bi–O$^-$ stretching vibrations of [BiO_3] triangles. All these bands which are related to Bi^{3+} become stronger as the content of Bi_2O_3 increases. The band positions and the corresponding assignments of Raman are given in Table 2 for all the glass compositions.

The IR and Raman spectra show that the vibrations of Bi_2O_3–ZnO–B_2O_3 glasses are mainly about the [BO_3], [BO_4], [BiO_3] and [BiO_6] units. The increase of the content of Bi_2O_3 in the present glass system transforms the structure into a bismuthate one formed by [BiO_6] and [BiO_3] groups, and more boron element in the glass have the trend to form [BO_3] units.

4.2. Viscosity and glass structure

The viscosity data summaries in Fig. 4 show nearly linear trends and can therefore be fitted over these restricted temperature ranges using the approximation of Arrhenian behaviour [24–26]:

$$\ln \eta = \frac{A + Ea}{RT} \quad (2)$$

where η is the viscosity (Pa s), A is the pre-exponential term, Ea is the activation energy of viscous flow, R is the gas constant (8.3145 J/K mol) and T is the absolute temperature.

Table 3 summarizes the values of Ea, A, and the temperature corresponding to $10^{5.5}$ and $10^{6.5}$ Pa s, it referred to as the glass's suitable sealing temperature range ($T_{5.5}$–$T_{6.5}$) of the investigated Bi_2O_3–ZnO–B_2O_3 glass. The value of pre-exponential term A and activation energy Ea show less difference and no-obvious regularity as the content of Bi_2O_3 increases. The value (calculated by using Eq. (1)) of $T_{5.5}$ and $T_{6.5}$ decreases as the content of Bi_2O_3 increases, respectively. The delta temp of $T_{5.5}$ and $T_{6.5}$ are all about 22–24 °C for each glass composition. Temperature suits for sealing is about 20 °C lower as the content of Bi_2O_3 changes from 37 to 42 mol%.

The viscosity of Bi_2O_3–ZnO–B_2O_3 glass may correlate to its glass structure. As the IR and Raman spectra show, the network of the investigated glass is formed by [BiO_3], [BO_3] and [BO_4]. The vibrations of [BiO_3] and [BO_3] become stronger as the content of Bi_2O_3 increases, [BO_4] on the contrary, and it made the glass structure more loosening. Then it is clear that the phenomenon of viscosity change for different glass compositions.

4.3. High-temperature microscope analysis

The wetting behaviors of the glasses to 439L stainless steel were investigated by observing the shape change of cylinder samples on 439L stainless steel plates with increasing temperature. The glasses A_1–A_5 showed quite a similar tendency in shape change. As is showed in Fig. 5, the shape of all the glass samples becomes smooth at $T_{6.5}$. It indicates that liquid phase appears in the samples. The shape of all the glass samples approaches semicircle when the temperature goes up to $T_{5.5}$. This means that the amount of liquid phase rises up.

The shape change of A_1–A_5 at about 452 °C is also found from Fig. 5, the surface curve of A_1 is not absolutely smooth, but A_5 is smooth almost. At the temperature (about 472 °C), the shape of A_1 has a tendency to circle shape, but A_5 is semicircle almost. It can prove that the structure of investigated Bi_2O_3–ZnO–B_2O_3 glasses becomes loosened as the content of Bi_2O_3 increases. Increasing

Table 3
The pre-exponential term A, activation energy Ea, the temperature corresponding to $10^{5.5}$ Pa s, $T_{5.5}$ and $10^{6.5}$ Pa s, $T_{6.5}$ as calculated using Eq. (2).

Sample	Ea (kJ mol^{-1})	A	$T_{5.5} \pm 2$ (°C)	$T_{6.5} \pm 2$ (°C)
A_1	475.67 ± 28.15	−61.74 ± 0.84	495	473
A_2	451.60 ± 26.25	−58.28 ± 0.82	492	468
A_3	468.60 ± 43.94	−61.69 ± 1.33	485	462
A_4	463.75 ± 36.97	−61.32 ± 1.13	480	458
A_5	472.15 ± 30.56	−63.25 ± 0.92	475	452

Bi_2O_3-concentration (37–42 mol%) can improve the wetting performance of investigated Bi_2O_3–ZnO–B_2O_3 glasses when bonded to 439L stainless steel plates at lower temperature.

5. Conclusion

The infrared and Raman spectra analysis shows that [BO_3], [BO_4], [BiO_3] and [BiO_6] are the main structure units of Bi_2O_3–ZnO–B_2O_3 glasses. The increase of Bi_2O_3 content transforms the structure into a bismuthate one formed by [BiO_6] and [BiO_3] groups and helps to a progressive conversion of [BO_4] to [BO_3] units. Glasses viscosities as the function of temperature were measured. With increasing Bi_2O_3-concentration (37–42 mol%), the viscosity decreases, this is due to the change of glass structure, increase of the content [BO_3] and [BiO_3] units, decrease of the content of [BO_4] tetrahedral which leads the loosening of structure. Temperature suited for sealing (calculated by using the approximation of Arrhenian behaviour) is about 20 °C lower as the content of Bi_2O_3 changes from 37 to 42 mol%. And high-temperature microscope also proves that the structure of investigated Bi_2O_3–ZnO–B_2O_3 glasses becomes loosened as the content of Bi_2O_3 increases.

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