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Approach to thermal properties and electronic polarizability from average single bond strength in $ZnO–Bi_2O_3–B_2O_3$ glasses

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ABSTRACT

The glass transition temperature (T_g), density, refractive index, Raman scattering spectra, and X-ray photoelectron spectra (XPS) for xZnO–yBi$_2$O$_3$–zB$_2$O$_3$ glasses ($x=10$–65, $y=10$–50, $z=25$–60 mol%) are measured to clarify the bonding and structure features of the glasses with large amounts of ZnO. The average electronic polarizability of oxide ions (α_{O2-}) and optical basicity (Λ) of the glasses estimated using Lorentz–Lorenz equation increase with increasing ZnO or Bi_2O_3 content, giving the values of $\alpha_{O2-}=1.963$ Å^3 and $\Lambda=0.819$ for 60ZnO–10Bi$_2$O$_3$–30B$_2$O$_3$ glass. The formation of B–O–Bi and B–O–Zn bridging bonds in the glass structure is suggested from Raman and XPS spectra. The average single bond strength (B_{M-O}) proposed by Dimitrov and Komatsu is applied to the glasses and is calculated using single bond strengths of 150.6 kJ/mol for Zn–O bonds in ZnO_4 groups, 102.5 kJ/mol for Bi–O bonds in BiO_6 groups, 498 kJ/mol for B–O bonds in BO_3 groups, and 373 kJ/mol for B–O bonds in BO_4 groups. Good correlations are observed between T_g and B_{M-O}, Λ and B_{M-O}, and T_g and Λ, proposing that the average single bond strength is a good parameter for understanding thermal and optical properties of $ZnO–Bi_2O_3–B_2O_3$ glasses.

1. Introduction

Zinc oxide (ZnO) is one of the important constituent components in the formation of oxide glasses, and in particular, it is known that glasses containing large amounts of ZnO have low melting temperatures. Because low melting glasses with large amounts of PbO, which have been used widely in various commercial devices, are now unfavorable from the environment point of view, the importance of low melting glasses with large amounts of ZnO and with no PbO is increasing largely. Indeed, for instance, $ZnO–B_2O_3$ glasses with high ZnO contents have been used as a sintering aid for the fabrication of low temperature co-fired ceramics [1,2]. Recently, Pinckney [3] succeeded in synthesizing of transparent crystallized glasses consisting of ZnO nanocrystals in $K_2O–ZnO–Al_2O_3–SiO_2$ glasses. Nagai et al. [4] succeeded in patterning lines consisting of ZnO crystals by laser irradiations in borosilicate glasses with a high ZnO content of 65.5 mol%. Glasses with high ZnO contents, therefore, are very attractive materials.

Many studies on the structure and properties of ZnO-containing glasses have been studied so far. However, information on the coordination and bonding states of Zn^{2+} ions in glasses with high ZnO contents is extremely poor. Almost 60 years ago, Sun [5] has proposed the bond energy criterion for the glass formation based on the dissociation energy of the oxides. He reported the data for the single bond strength of a chemical bond M–O in an oxide MO_x obtained by dividing the dissociation energy of the oxide by the coordination number of the metal M. The data reported by Sun are well known among the glass scientists, because they provide a good basis for separating oxides into glass-formers, intermediates and modifiers. Recently, based on Sun's approach, Dimitrov and Komatsu [6] have proposed that the average single bond strength B_{M-O} of binary glass with general formula $xA_pO_q(1-x)B_rO_s$ could be expressed by the following equation:

$$B_{M-O}=xB_{A-O}+(1-x)B_{B-O} \tag{1}$$

where x is the mole fraction of A_pO_q, B_{A-O} and B_{B-O} are single bond strengths of M–O in the corresponding individual oxide. They demonstrated that there is a good correlation among electronic oxide polarizability (i.e., optical basicity) and average single bond strength of several oxide glasses including $La_2O_3–P_2O_5$, $Na_2O–SiO_2$, $PbO–SiO_2$, $Na_2O–GeO_2$, $R_2O–TeO_2$ (R=Li, Na, K), $Bi_2O_3–B_2O_3$, $Sb_2O_3–B_2O_3$ glasses as well as some vanadate glasses [6–10]. That is, in general the electronic oxide polarizability increases with decreasing single bond strength of glasses. Since the pioneering works by Duffy and Ingram [11,12], it has been recognized that electronic polarizability is one of the most important properties of materials in the field of optics and electronics. The data reported by Dimitrov and Komatsu [6–10] propose a close link between optical

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and thermodynamic properties of glasses. It is of interest to approach thermal properties and electronic polarizability of glasses with high ZnO contents from the point of view of average single bond strength.

In this study, we focus our attention on ZnO–Bi_2O_3–B_2O_3 glasses containing ZnO contents of 10–60 mol%. Since the first report by Dumbaugh [13] on Bi_2O_3-based glasses, it is well established that the addition of Bi_2O_3 has a strong effect on lowering of melting temperatures in glasses. It is also noted that glasses containing Bi_2O_3 exhibit large third order nonlinear optical susceptibilities $\chi^{(3)}$ of the order 10^{-11} esu [14,15]. Glasses based on the ZnO–Bi_2O_3–B_2O_3 system are, therefore, very interesting in the field of solid state materials science and technology. In the present study, we measured the glass transition temperature, density, refractive index, Raman scattering spectra, and X-ray photoelectron spectra (XPS) for ZnO–Bi_2O_3–B_2O_3 glasses and tried to characterize their thermal properties and electronic polarizability (optical basicity) from the point of view of average single bond strength.

2. Experimental

The chemical compositions of ZnO–Bi_2O_3–B_2O_3 glasses prepared in the present study are given in Table 1. Glasses were prepared using a conventional melt quenching technique. Commercial powders of reagent grade ZnO, Bi_2O_3, and H_3BO_3 were melted in a platinum crucible at 1000 °C for 30 min in an electric furnace. The melts were poured onto an iron plate and pressed to a thickness of ~1.5 mm by another iron plate. Glass transition temperatures (T_g) were determined using differential thermal analyses (DTA) at a heating rate of 10 K/min. Densities of glasses were determined with the Archimedes method using distilled water as an immersion liquid. Refractive indices at a wavelength of 632.8 nm (He–Ne laser) were measured at room temperature with a prism coupler (Metricon Model 2010).

Raman scattering spectra at room temperature for the glasses were measured with a laser microscope (Tokyo Instruments Co., Nanofinder) operated at Ar^+ laser (wavelength: λ=488 nm). In this apparatus, the data below 250 cm^{-1} cannot be measured due to the use of an edge filter. XPS measurements were carried out with a *JEOL JPS-9010TR* electron spectrometer which has Al conical anode for charge control. Non-monochromatic 240 W Mg$K\alpha$ X-ray provided the excitation radiation. During experiments the pressure inside the analyzer chamber was about 10^{-7} Pa. The drift of the electron binding energy due to surface charging effect was calibrated by utilizing the C1*s* peak (binding energy=284.6 eV) of the contamination of the pumping oil at the sample introduction chamber.

Table 1
Compositions, glass transition temperature T_g, density d, refractive index at 642.8 nm n, molar volume V_m, and atom packing density V_p for $ZnO-Bi_2O_3-B_2O_3$ glasses. The experimental uncertainties of T_g, d, and n are ± 2 °C, ± 0.003 g/cm³, and ± 0.001, respectively.

Composition (mol%)				T_g (°C)	d (g/cm³)	n	V_m (cm³/mol)	V_p
Sample	ZnO	Bi_2O_3	B_2O_3					
Glass A	30	10	60	515	4.209	1.748	26.80	0.583
Glass B	40	10	50	499	4.529	1.784	25.17	0.574
Glass C	50	10	40	471	4.842	1.815	23.78	0.557
Glass D	60	10	30	449	5.152	1.851	22.58	0.534
Glass E	65	10	25	440	5.292	1.870	22.10	0.519
Glass F	30	20	50	482	5.445	1.895	27.99	0.578
Glass G	40	20	40	462	5.688	1.933	27.01	0.555
Glass H	50	20	30	435	5.964	1.968	25.95	0.532
Glass I	20	30	50	440	5.993	1.986	31.85	0.563
Glass J	30	30	40	421	6.192	2.021	31.01	0.539
Glass K	40	30	30	398	6.497	2.059	29.75	0.522
Glass L	20	40	40	397	6.798	2.095	33.91	0.545
Glass M	10	50	40	376	7.151	2.155	37.61	0.537

3. Results and discussion

3.1. Glass transition temperature of glasses

The melt-quenched samples for all compositions of ZnO–Bi_2O_3–B_2O_3 examined in this study are optically transparent. The amorphous state in the as-quenched samples was confirmed from XRD patterns, in which halo patterns were observed. The DTA patterns for xZnO–10Bi_2O_3–(90−x)B_2O_3 glasses with x=40–60 are shown in Fig. 1 as examples. Endothermic peaks due to the glass transition were clearly observed, giving the values of T_g=499 °C for the glass with x=40, T_g=471 °C for the glass with x=50, and T_g=449 °C for the glass with x=60. In the glasses with x=50 and 60, exothermic peaks due to the crystallization are observed, giving the crystallization peak temperatures (T_p) of T_p=673 °C for the glass with x=50 and T_p=593 °C for the glass with x=60. These results indicate that thermal stability against crystallization in xZnO–10Bi_2O_3–(90−x)B_2O_3 glasses decreases with the substitution of ZnO for B_2O_3. The endothermic peak due to the glass transition was observed in other glasses, and the values of T_g estimated from DTA curves are given in Table 1. The glasses of ZnO–Bi_2O_3–B_2O_3 show the values of T_g=376–515 °C, and it is seen that the values of T_g decrease with increasing ZnO or Bi_2O_3 content and decreasing B_2O_3 content. For instance, the glass of 40ZnO–20Bi_2O_3–40B_2O_3 has the value of T_g=462 °C, and the glass of 20ZnO–40Bi_2O_3–40B_2O_3 shows the value of T_g=397 °C. It should be, therefore, pointed out that Bi_2O_3 has a stronger effect for lowering the glass transition temperature, i.e., weakening the glass network structure, of ternary ZnO–Bi_2O_3–B_2O_3 glasses compared with ZnO.

The values of density, d, and refractive index, n, at room temperature for the glasses are given in Table 1. It is seen that both values increase with increasing ZnO or Bi_2O_3 content and decreasing B_2O_3 content. As similar to the glass transition temperature, Bi_2O_3 has a stronger effect for the density and refractive index compared with ZnO. For instance, the glass of 40ZnO–20Bi_2O_3–40B_2O_3 has the values of d=5.688 g/cm³ and n=1.933, and the glass of 20ZnO–40Bi_2O_3–40B_2O_3 shows the values of d=6.798 g/cm³ and n=2.155.

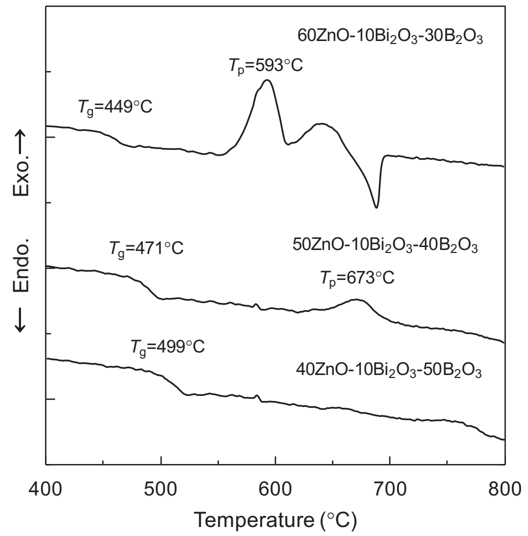

Fig. 1. DTA patterns for $xZnO-10Bi_2O_3-(90-x)B_2O_3$ glasses with x=40–60. Heating rate was 10 K/min.

3.2. Electronic polarizability of glasses

The electronic polarizabilities and optical basicities of ZnO–Bi_2O_3–B_2O_3 glasses were estimated using the following equations [16–19]:

$$R_m = \left[\frac{(n^2-1)}{(n^2+2)}\right]\left(\frac{M}{d}\right) = \left[\frac{(n^2-1)}{(n^2+2)}\right]V_m = \frac{4\pi\alpha_m N}{3} \tag{2}$$

$$\alpha_{O2-}(n) = \left[\frac{R_m}{2.52} - \sum \alpha_i\right](N_{O2-})^{-1} \tag{3}$$

$$\Lambda = 1.67\left(1 - \frac{1}{\alpha_{O2-}}\right) \tag{4}$$

where R_m is the molar refraction, M is the molecular weight, V_m is the molar volume, α_m is the molar polarizability, N is the Avogadro's number, $\alpha_{O2-}(n)$ is the average electronic polarizability of oxide ions, $\sum\alpha_i$ denotes molar cation polarizability, N_{O2-} denotes the number of oxide ions in the chemical formula, and Λ is the so-called optical basicity of the oxide medium. For example, the number of oxide ions (N_{O2-}) in 30ZnO–$10Bi_2O_3$–$60B_2O_3$ glass (mol%) is 2.4. Eq. (2) is the so-called Lorentz–Lorenz equation giving the relationship between molar refraction (R_m) and refractive index (n). Eq. (3) proposed by Dimitrov and Sakka [17] gives the electronic polarizability of oxide ions ($\alpha_{O2-}(n)$) in oxide materials by subtracting the cation polarizability ($\sum\alpha_i$) from the molar polarizability (α_m). Eq. (4) proposed by Duffy [16] gives an intrinsic relationship between electronic polarizability of the oxide ions and so-called optical basicity of the oxide medium (Λ). The optical basicity of an oxide medium as proposed by Duffy and Ingram [11,12] is a numerical expression of the average electron donor power of the oxide species constituting the medium. Because increased oxide ion polarizability means stronger electron donor ability of oxide ions, the physical background of the oxide ion polarizability and optical basicity is naturally the same.

Using Eqs. (2)–(4), we estimated the values of α_m, α_{O2-} and Λ of ZnO–Bi_2O_3–B_2O_3 glasses prepared in the present study, and the results are shown in Table 2. The values of α_{Zn}=0.283 Å^3 for Zn^{2+} ions, α_{Bi}=1.508 Å^3 for Bi^{3+} ions and α_B=0.002 Å^3 for B^{3+} ions are used [17]. As can be seen in Table 2, the average electronic polarizability of oxide ions and optical basicity in ZnO–Bi_2O_3–B_2O_3 glasses increase with increasing ZnO or Bi_2O_3 or with the decease of B_2O_3 content. As reported by Dimitrov and Sakka [17], the simple oxides of ZnO, Bi_2O_3 and B_2O_3 have the following values for optical basicity: Λ=1.03 for ZnO, Λ=1.19 for Bi_2O_3, and Λ=0.43 for B_2O_3, respectively. It is, therefore, expected that the degree of basicity (electron donor ability of oxide ions) in these simple oxides is in the order: $B_2O_3 \ll ZnO < Bi_2O_3$. The general trend that the electronic polarizability of oxide ions in ZnO–Bi_2O_3–B_2O_3 glasses increases with the substitution of ZnO or Bi_2O_3 for B_2O_3 seems to be reasonable.

Table 2
Molar refractivity R_m, molar polarizability α, oxide ion polarizability α_{O2-}, optical basicity Λ, and average single bond strength B_{M-O} calculated by using Eq. (5) for $ZnO-Bi_2O_3-B_2O_3$ glasses. The values of N_4 were taken from Ref. [34].

Glass	R_m	α	α_{O2-} (Å^3)	Λ	B_{M-O} (kJ/mol)	N_4
Glass A	10.90	4.322	1.640	0.652	331	0.305
Glass B	10.60	4.203	1.722	0.700	300	0.314
Glass C	10.31	4.087	1.822	0.754	270	0.295
Glass D	10.10	4.004	1.963	0.819	239[a]	–
Glass E	10.04	3.981	2.057	0.858	223[a]	–
Glass F	12.97	5.145	1.858	0.771	294	0.331
Glass G	12.88	5.109	1.997	0.834	265	0.308
Glass H	12.70	5.035	2.146	0.892	237	0.227
Glass I	15.78	6.256	2.037	0.850	288	0.350
Glass J	15.72	6.235	2.187	0.906	259	0.316
Glass K	15.44	6.124	2.322	0.951	231	0.243
Glass L	17.99	7.130	2.259	0.931	255	0.314
Glass M	20.63	8.182	2.374	0.967	250	0.314

[a] These values were calculated under the assumption of N_4=0.3.

3.3. Raman scattering spectra of glasses

In order to get information on structural features of ZnO–Bi_2O_3–B_2O_3 glasses, Raman scattering spectra at room temperature for the glasses were measured. Some data obtained are shown in Figs. 2–4. All glasses show some common broad peaks at ~350, 600, 720, 920, and 1150–1450 cm^{-1}. In xZnO–$10Bi_2O_3$–$(90-x)B_2O_3$ glasses with x=40–60 (Fig. 2), the position and intensity of the peak at ~350 cm^{-1} are almost the same irrespective of the ratio of ZnO/B_2O_3, and the intensity of the peaks at 600 and 920 cm^{-1} increases with increasing ZnO content. For the very broad peak at 1150–1450 cm^{-1}, the center position tends to shift towards lower wavenumbers with increasing ZnO content. In xZnO–$(60-x)Bi_2O_3$–$40B_2O_3$ glasses with x=30–50 (Fig. 3), the intensity of the peak at ~350 cm^{-1} increases with increasing Bi_2O_3 content. The intensity of the peaks at 600 and

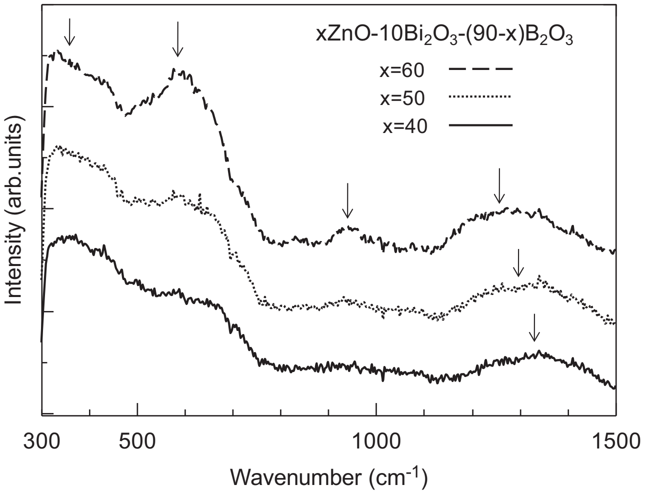

Fig. 2. Raman scattering spectra at room temperature for xZnO – $10Bi_2O_3$ – $(90-x)$ B_2O_3 glasses with x=40–60.

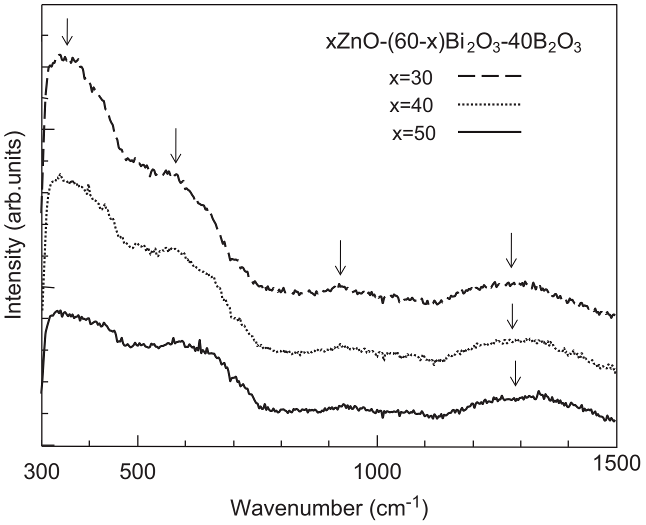

Fig. 3. Raman scattering spectra at room temperature for xZnO – $(60-x)Bi_2O_3$ – $40B_2O_3$ glasses with x=30–50.

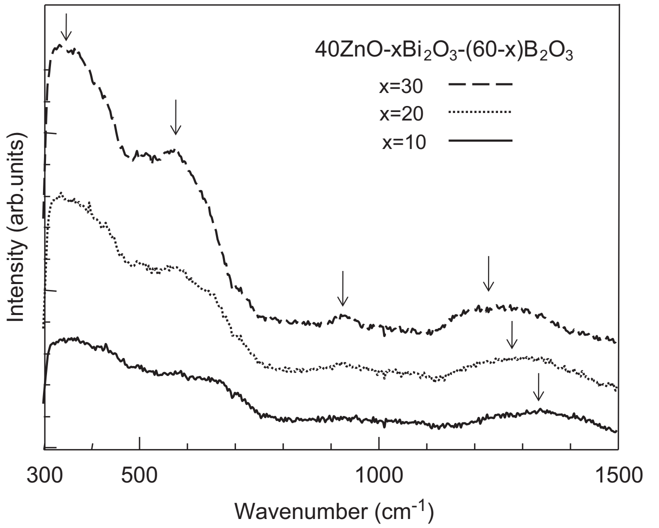

Fig. 4. Raman scattering spectra at room temperature for $40ZnO-xBi_2O_3-(60-x)B_2O_3$ glasses with $x=10–30$.

920 cm^{-1} are almost the same irrespective of the ratio of ZnO/Bi_2O_3. The center position of the broad peak at 1150–1450 cm^{-1} tends to shift slightly towards lower wavenumbers with increasing Bi_2O_3 content. In $40ZnO–xBi_2O_3–(60-x)B_2O_3$ glasses with $x=10–30$ (Fig. 4), the intensity of the peaks at ~350, 600, and 920 cm^{-1} increases with increasing Bi_2O_3 content. The center position of the broad peak at 1150–1450 cm^{-1} tends to shift clearly towards lower wavenumbers with increasing Bi_2O_3 content. Similar features in Raman scattering spectra were observed in other glasses prepared in this study. The features of Raman scattering spectra for $ZnO–Bi_2O_3–B_2O_3$ glasses are, therefore, summarized as follows: (1) the peak intensity at ~350 cm^{-1} increases with increasing Bi_2O_3 content, (2) the peak intensity at ~600 and 920 cm^{-1} increases with increasing ZnO and Bi_2O_3 contents, (3) the center position of the broad peak at 1150–1450 cm^{-1} tends to shift towards lower wavenumbers with increasing ZnO and Bi_2O_3 contents.

It is possible to assign the observed bands in the spectra in accordance with the approach introduced by Lines [20] and Lines et al. [21,22] about the intensity of Raman scattering in glasses containing heavy metal oxides. According to Lines et al. [20,21], the Raman spectra of such glasses are interpreted as being of four types: acoustic Raman (AR) peaks occur at lowest values of Raman shift ($\Delta\nu$) usually in the $\Delta\nu=50–150$ cm^{-1} regions; frequently overlapping heavy metal (HM) peaks in the $\Delta\nu=70–160$ cm^{-1} region; the bridged anion (BA) peaks occur in the intermediate region about $\Delta\nu=350–600$ cm^{-1} and the highest values of about $\Delta\nu=650–920$ cm^{-1} are the non-bridging (NBA) peaks. Furthermore, for BA peaks the modes involved are derived from symmetric stretch anion motion in angularly constrained cation–anion–cation configurations, i.e., C–A–C, or their C–A–C′ equivalents if two different cations C and C′ are involved. For NBA peaks, it is the asymmetric stretch anion motion in C′–A–C configurations that is significant, and the modes with the strongest NBA Raman intensity usually involve partially covalent and partially ionic linkages C–A–C [22]. It is expected that the strongest BA-type Raman intensities will occur in glasses with large concentration of angularly constrained anion bridges involving highly polarizable bonds, small anion mass, large cation and anion valencies, and low Raman frequency shift. Large NBA intensities are expected in the presence of large concentrations of C′–A–C bridges involving C′–A and C–A bonds of very different polarizabilities, so that mixtures of about equal amounts of very different cations will generally favor large NBA Raman features.

On this basis, we can interpret the Raman scattering spectra (Figs. 2–4) obtained for $ZnO–Bi_2O_3–B_2O_3$ glasses in this study as follows: (1) the band at 350 cm^{-1} can be connected with symmetric stretch anion motion in Bi–O–Bi bonds between BiO_6 groups; (2) the band at 600 cm^{-1} could be assigned to symmetric stretch anion motion in B–O–Bi and B–O–Zn bonds; (3) the band at 920 cm^{-1} can be related mainly to asymmetric stretch anion motion in B–O–Bi and B–O–Zn bonds; (4) the band at 1450–1150 cm^{-1} can be assigned to asymmetric stretching vibration of B–O bonds in BO_3 groups. The shift of this peak to lower frequencies with increasing of Bi_2O_3 or ZnO content is connected with the formation of B–O–Bi and B–O–Zn bridging bonds in the glass structure.

The Raman scattering spectra shown in Figs. 2 to 4, in particular the peaks at ~920 and 1150–1450 cm^{-1}, suggest that both BO_3 to BO_4 units are present in $ZnO–Bi_2O_3–B_2O_3$ glasses [23]. It has been reported that vibration frequencies of BiO_3 groups in glasses are around 840–860 cm^{-1} [24,25]. Because no Raman bands have been observed clearly at around 850 cm^{-1} in Figs. 2–4, it is difficult to find evidence for existence of BiO_3 groups in $ZnO–Bi_2O_3–B_2O_3$ glasses. It is generally recognized that ZnO may participate in the glass network as a network modifier and also as a network-former. Meera and Ramakrishna [26] stated in their review paper on Raman spectra of borate glasses that the role of ZnO in network modification is not clearly understood, although the Raman data are consistent with the network-forming tendency of ZnO. Unfortunately, clear information on the oxygen coordination state of Zn^{2+} ions in $ZnO–Bi_2O_3–B_2O_3$ glasses has not been obtained from the Raman scattering spectra in the present study.

3.4. XPS spectra for the glasses

The XPS spectra at room temperature of B1*s*, Zn2$p_{3/2}$, Bi4*f*, and O1*s* core level regions for $xZnO–10Bi_2O_3–(90-x)B_2O_3$ glasses with $x=30–65$ are shown in Figs. 5–8. The peak attributed to B1*s* binding energy (E_B) at E_B~191.5 eV shifts towards lower binding energies with decreasing B_2O_3 content or increasing ZnO content as shown in Fig. 5. This behavior in the B1*s* binding energy is consistent with

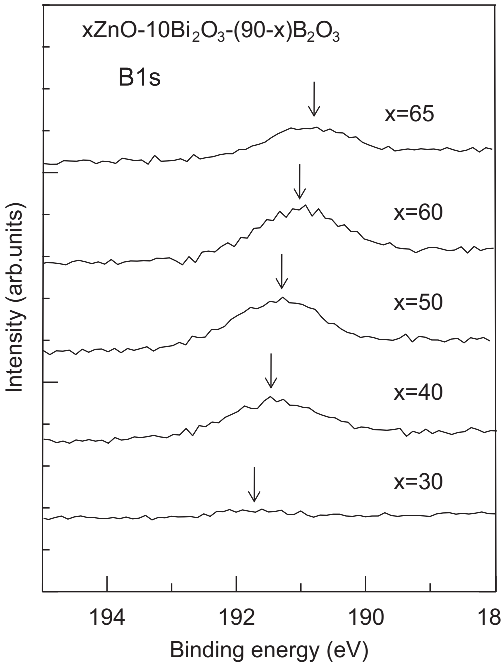

Fig. 5. XPS spectra at room temperature of B1*s* core level regions for $xZnO-10Bi_2O_3-(90-x)B_2O_3$ glasses with $x=30–65$.

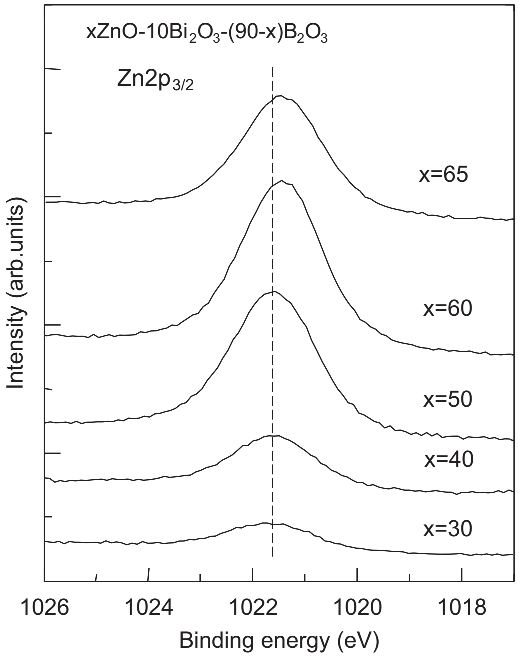

Fig. 6. XPS spectra at room temperature of Zn2$p_{3/2}$ core level regions for xZnO – 10Bi$_2$O$_3$ – (90 – x)B$_2$O$_3$ glasses with x=30–65.

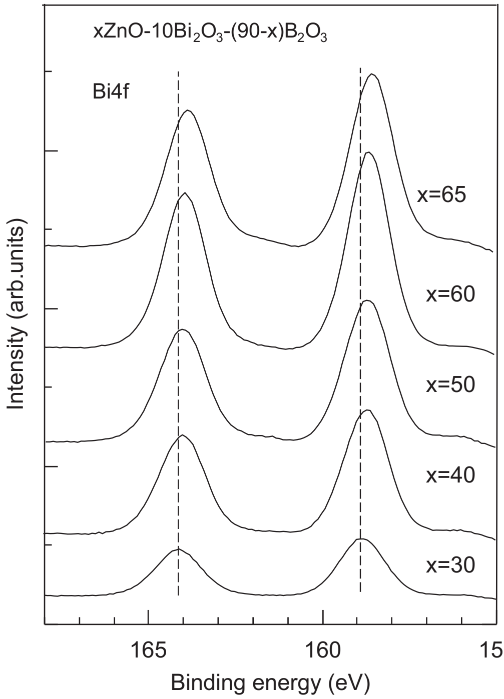

Fig. 7. XPS spectra at room temperature of Bi4f core level regions for xZnO – 10Bi$_2$O$_3$ – (90 – x)B$_2$O$_3$ glasses with x=30–65.

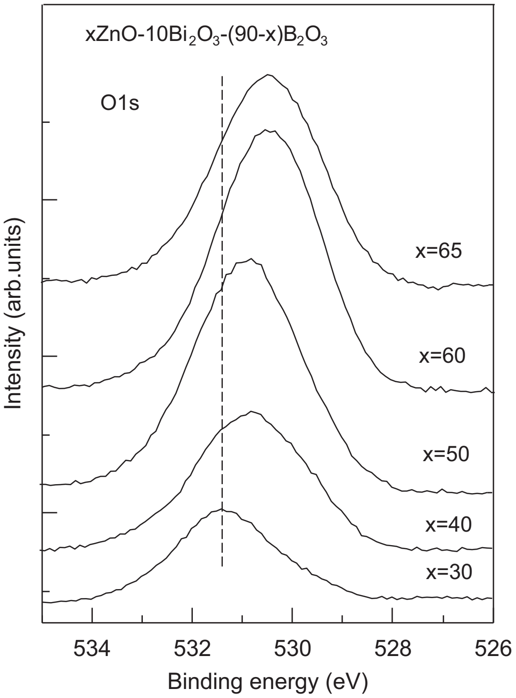

Fig. 8. XPS spectra at room temperature of O1s core level regions for xZnO – 10Bi$_2$O$_3$ – (90 – x)B$_2$O$_3$ glasses with x=30–65.

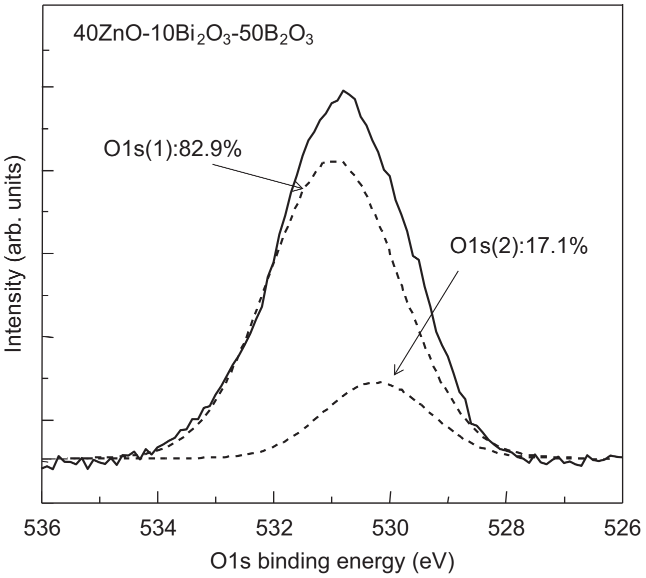

Fig. 9. XPS spectrum at room temperature of O1s core level regions for 40ZnO – 10Bi$_2$O$_3$ – 50B$_2$O$_3$ glass.

that in the Raman peak at 1150–1450 cm^{-1} (Fig. 2). That is, both B1s binding energy and Raman peak at 1150–1450 cm^{-1} shift towards lower energy and wavenumber, respectively, with the substitution of ZnO for B$_2$O$_3$. As can be seen in Fig. 6, the peak attributed to Zn2$p_{3/2}$ binding energy has almost the same position of E_B ~ 1021.6 eV for the glasses with x=30–50, but shift slightly towards lower binding energies for the glasses with x=60 and 65. The peaks attributed to Bi4f binding energy at E_B ~ 159 and ~ 164 eV shift slightly towards lower binding energies with the substitution of ZnO for B$_2$O$_3$ as shown in Fig. 7, although the Bi$_2$O$_3$ content is fixed to 10 mol%. Honma et al. [27] reported that the Bi4f peak in Bi$_2$O$_3$–B$_2$O$_3$ glasses shift towards lower binding energy with increasing Bi$_2$O$_3$ content.

The peak attributed to O1s binding energy at E_B ~ 531 eV shifts towards lower binding energies with the substitution of ZnO for B$_2$O$_3$ as shown in Fig. 8. Because the O1s XPS spectra are very broad and asymmetric, we tried to decompose the peaks, where the spectra were fitted with a sum of Gaussian curves by means of least square method. The fitting result for 40ZnO–10Bi$_2$O$_3$–50B$_2$O$_3$ glass is shown in Fig. 9, as an example. The spectrum was decomposed into two components denoted as O1s(1) and O1s(2) with a good fitting quality, giving the binding energies of $E_B = 531.0$ eV for the O1*s*(1) component (high binding energy) and $E_B = 530.2$ eV for the O1*s*(2) component (low binding energy). The glass of 30ZnO–10Bi_2O_3–60B_2O_3 gives the values of $E_B = 531.5$ eV for O1*s*(1) and $E_B = 530.3$ eV for O1*s*(2), and other glasses with $x = 50$, 60, and 65 show almost the same values of $E_B = 531.0$–531.1 eV for O1*s*(1) and $E_B = 530.1$–530.2 eV for O1*s*(2). The fraction of O1*s*(2), i.e., the area ratio of O1*s*(1) and O1*s*(2) components in XPS spectra, was found to increase with the substitution of ZnO for B_2O_3, and the data are given in Table 3. For instance, the glass of 60ZnO–10Bi_2O_3–30B_2O_3 gives the O1*s*(2) fraction of 0.446. These data indicate that basically two kinds of oxygen having high O1*s*(1) and low O1*s*(2) binding energies are present in ZnO–Bi_2O_3–B_2O_3 glasses.

Matsumoto et al. [28] reported that the O1*s* XPS spectra of alkali and alkaline earth borate glasses at comparatively low modifier oxide contents show only single bridging oxygen (BO) peak which is shifted to lower binding energy with increasing modifier content and proposed that three types of BO atoms, i.e., B(3)–O–B(3), B(3)–O–B(4), and B(4)–O–B(4), are not separated in O1s spectra, where B(3) and B(4) are three (BO_3) and four (BO_4) coordinated boron atoms, respectively. It is, therefore, considered that the O1s(1) component in ZnO–Bi_2O_3–B_2O_3 glasses examined in the present study is attributed to the oxygen in B(3)–O–B(3) and B(3)–O–B(4) bonds and the O1*s*(2) component is related to the oxygen in B–O–Zn and B–O–Bi bonds. Considering the shift towards lower binding energies in Zn2$p_{3/2}$ and Bi4*f* peaks (Figs. 6 and 7), Zn–O–Bi bonds might be also formed.

The increase in the fraction of O1*s*(2) component in *x*ZnO–10Bi_2O_3–$(90-x)B_2O_3$ glasses with increasing ZnO content shown in Table 3 means the decrease in the mean O1*s* binding energy due to the substitution of ZnO for B_2O_3. The values of the mean O1*s* binding energy calculated from the fraction of O1*s*(1) and O1*s*(2) are given in Table 3. The XPS spectra shown in Figs. 5–8 for *x*ZnO–10Bi_2O_3–$(90-x)B_2O_3$ glasses, therefore, indicate that all binding energies corresponding to the B1*s*, Zn2$p_{3/2}$, Bi4*f*, and O1*s* core level tend to decrease with increasing ZnO or the substitution of ZnO for B_2O_3. Dimitrov and Komatsu [29] suggested that outermost core-level binding energy in simple oxides can be used for relative measuring the cation polarizability. That is, in general, cation polarizability increases with decreasing metal (nonmetal) binding energy. They also found that a decreasing of metal binding energy in XPS spectra of simple oxides is accompanied with decreasing of O1*s* binding energy, that is related to increased optical basicity [29]. A relation between metal binding energy and O1*s* binding energy has been established in Sb_2O_3–B_2O_3 and Bi_2O_3–B_2O_3 glasses [27,30]. It should be pointed out that such a relation (trend) has been observed even in ZnO–Bi_2O_3–B_2O_3 glasses. We assume that the observed chemical shift of both O1*s* and metal binding energies toward lower binding energy with increasing basicity can be regarded as experimental proof for interaction between valence orbitals of metal and oxide ions leading to the formation of *M*–O chemical bonds (*M*=Zn, Bi and B) in the glass structure. Therefore, the chemical shift of the mean O1*s* binding energy to lower values is indication of rise in the negative charge born by an averaged oxide ion. At the same time a back electron donation from the oxide ions to metal ions is a possible reason for the increase of electron density around metal ions and a decrease of metal binding energy in XPS spectra. This is apparently equivalent to an increase in covalency of Zn–O and Bi–O bonds.

Table 3
Values of O1*s*(1) and O1*s*(2) binding energies, the fraction (area ratio) of O1*s*(2) component against f the total component (O1*s*(1)+O1*s*(2)), and mean O1*s* binding energy obtained in XPS spectra at room temperature for *x*ZnO – 10Bi_2O_3 – $(90-x)B_2O_3$ glasses. The experimental uncertainty in the binding energy is less than ±0.1 eV.

Glass (mol%)	O1*s*(1) (eV)	O1*s*(2) (eV)	Fraction of O1*s*(2)	Mean O1*s* (eV)
$x=30$	531.53	530.33	0.174	531.32
$x=40$	530.96	530.23	0.171	530.83
$x=50$	531.09	530.24	0.252	530.87
$x=60$	530.96	530.06	0.446	530.56
$x=65$	530.96	530.06	0.469	530.53

It has been well established that there is a good correlation between mean O1*s* binding energy and optical basicity in various oxide glasses, i.e., glasses with high O1*s* binding energies show low optical basicities [27,29–33]. The values of the optical basicity of *x*ZnO–10Bi_2O_3–$(90-x)B_2O_3$ glasses (Table 2) are plotted in Fig. 10 as a function of the mean O1*s* binding energy, in which the data on xBi_2O_3–$(100-x)B_2O_3$ glasses with $x = 25$–65 reported by Honma et al.[27] are also plotted. It is seen that the optical basicity of the glasses in both systems increases with increasing ZnO or Bi_2O_3 contents.

3.5. *Evaluation of average single bond strength of glasses*

The purpose of the present study is to approach thermal properties and electronic polarizability (optical basicity) in ZnO–Bi_2O_3–B_2O_3 glasses from the parameter (concept) of average single bond strength. According to Sun [5], single bond strength of a chemical bond *M*–O in an oxide MO_x is obtained by dividing the dissociation energy of the oxide by the coordination number of the metal *M*. And, therefore, to evaluate the average single bond strength of ZnO–Bi_2O_3–B_2O_3 glasses, i.e., $B_{M\text{–}O}$ in Eq. (1), information on the coordination states of Zn^{2+}, Bi^{3+}, and B^{3+} ions is needed.

Very recently, Ida et al. [34] measured and analyzed ^{11}B magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra of ZnO–Bi_2O_3–B_2O_3 glasses with the content of ZnO = 0–60 mol% and reported the fraction of BO_4 structural units. The values reported, i.e., $N_4/(N_4+N_3)$, are given in Table 2, where N_4 and N_3 are the fractions of BO_4 and BO_3 units, respectively. It is seen that the fraction of BO_4 units in ZnO–Bi_2O_3–B_2O_3 glasses examined in this study is in the range of $N_4 = 0.227$–0.350. The Raman scattering spectra shown in Figs. 2–4 indicate at least the presence of BiO_6 units in ZnO–Bi_2O_3–B_2O_3 glasses, but there is no evidence for

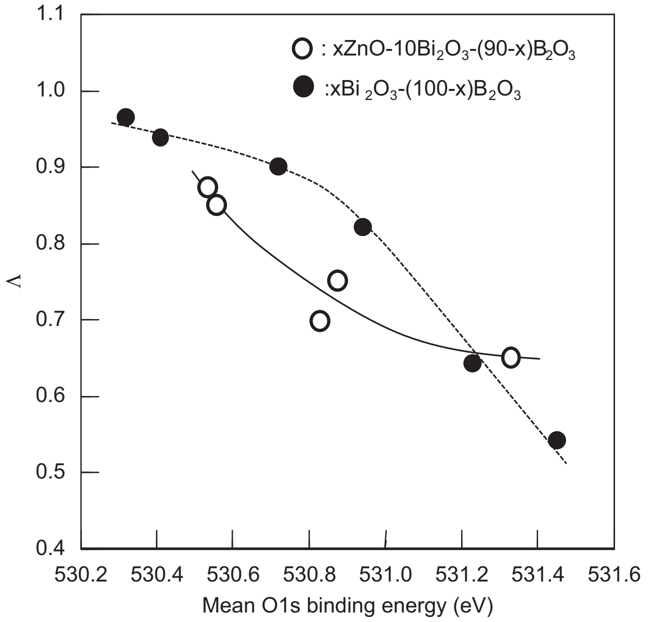

Fig. 10. Correlation between mean O1*s* binding energy and optical basicity in *x*ZnO – 10Bi_2O_3 – $(90-x)B_2O_3$ glasses with $x = 30$–65. The data on $xBi_2O_3 - (100-x)B_2O_3$ glasses with $x = 25$–65 reported by Honma et al. [27] are also included.

existence of BiO_3 groups in $ZnO–Bi_2O_3–B_2O_3$ glasses. It has been proposed from IR, Raman spectra and X-ray diffraction analysis that the coordination number of Bi^{3+} ions in $Bi_2O_3–B_2O_3$ glasses does not change and remains high values of around six independent of glass composition, i.e., BiO_6 structural units [15,35]. Unfortunately, clear information on the oxygen coordination state of Zn^{2+} ions in $ZnO–Bi_2O_3–B_2O_3$ glasses has not been obtained in the present study. However, ZnO_4 structural units would be probably the most preferable groups in the structure of ZnO-containing oxide glasses. Sakida et al. [36] have reported from X-ray diffraction analyses that the coordination number of Zn atoms in the structure of $ZnO–TeO_2$ glasses decreases from 5.3 to 3.9 as ZnO content increases from 10 to 40 mol%. Raju et al. [37] proposed from infra-red (IR) and Raman scattering spectra that Zn^{2+} ions take the tetrahedral coordinated state ZnO_4 as network formers in $20ZnO–20ZnF_2–60B_2O_3$ glass.

On the basis described in the above, we can assume the presence of ZnO_4, BiO_6, BO_3 and BO_4 groups only in the structure of $ZnO–Bi_2O_3–B_2O_3$ glasses. According to the equation proposed by Dimitrov and Komatsu [6] based on the Sun's approach, the average single bond strength $B_{M–O}$ of ternary $ZnO–Bi_2O_3–B_2O_3$ glasses could be, therefore, expressed as follows:

$$B_{M-O} = xB_{Zn-O^{(4)}} + yB_{Bi-O^{(6)}} + (1-x-y)[N_3 B_{B-O^{(3)}} + N_4 B_{B-O^{(4)}}] \qquad (5)$$

where x and y are the mole fractions of ZnO and Bi_2O_3, respectively. $B^{(4)}_{Zn-O}$ and $B^{(6)}_{Bi-O}$ are the single bond strength of Zn–O and Bi–O bonds in ZnO_4 and BiO_6 groups, respectively, and $B^{(3)}_{B-O}$ and $B^{(4)}_{B-O}$ are the single bond strength of B–O bonds in the BO_3 and BO_4 groups, respectively. (Note that the coordination number of the cation is shown in brackets as superscript.)

According to Sun [5], the single bond strength of B–O bond in B_2O_3 oxide, B_{B-O}, is 498 kJ/mol for BO_3 structural units and 373 kJ/mol for BO_4 structural units, and that of Zn–O bond in ZnO, $B^{(4)}_{Zn-O}$, is 150.6 kJ/mol for ZnO_4 units. Furthermore, the single bond strength of Bi–O bond in Bi_2O_3, i.e., $B^{(6)}_{Bi-O}$, is assumed to be 102.5 kJ/mol for BiO_6 units, because the dissociation energy of Bi_2O_3 is 615 kJ/mol [38]. From the values of $B^{(4)}_{Zn-O}=150.6$ kJ/mol, $B^{(6)}_{Bi-O}=102.5$ kJ/mol, $B^{(3)}_{B-O}=498$ kJ/mol, and $B^{(4)}_{B-O}=373$ kJ/mol, and the fraction (N_4) of BO_4 units shown in Table 2, the average single bond strength of B_{M-O} for $ZnO–Bi_2O_3–B_2O_3$ glasses were calculated using Eq. (5), and the results are shown in Table 2. It is seen that the average single bond strength decreases with the substitution of ZnO or Bi_2O_3 for B_2O_3, because the single bond strength is in the order of Bi_2O_3 (102.5 kJ/mol) < ZnO (150.6 kJ/mol) ≪ B_2O_3 (373 or 498 kJ/mol).

3.6. Relationship between properties and average single bond strength

The values of the glass transition temperature (T_g) for $ZnO–Bi_2O_3–B_2O_3$ glasses are plotted as a function of the average single bond strength $B_{M–O}$ in Fig. 11. It is seen that the glass transition temperature increases with increasing $B_{M–O}$. Its relation depends on the glass series. The relationship between the optical basicity (Λ) and $B_{M–O}$ is also shown in Fig. 12, indicating that the value of Λ decreases with increasing $B_{M–O}$ and its relation depends on the glass series as similar to the case of the glass transition temperature. The glass transition temperature is a measure of the thermal stability of structural network, and thus glasses constructing with strong chemical bonding would be expected to have high glass transition temperatures. Considering the concept and nature of optical basicity proposed by Duffy and Ingram [11,12], it is expected that glasses having a strong covalent nature in their chemical bonding states would show small optical basicities. The results shown in Figs. 11 and 12 would be, therefore, reasonable.

As can be seen in Table 1, the glasses of $50ZnO–10Bi_2O_3–40B_2O_3$ and $10ZnO–50Bi_2O_3–40B_2O_3$ have the values of $T_g=499$ and 376 °C, respectively, indicating a more larger effect of Bi_2O_3 on lowering T_g compared with ZnO. The glasses of $40ZnO–20Bi_2O_3–40B_2O_3$ and $40ZnO–30Bi_2O_3–30B_2O_3$ have the values of $T_g=462$ and 398 °C, respectively, indicating an extremely large effect of Bi_2O_3 on lowering T_g in $ZnO–Bi_2O_3–B_2O_3$ glasses. These compositional dependences of T_g in $ZnO–Bi_2O_3–B_2O_3$ glasses are well explained from the order of Bi_2O_3 < ZnO ≪ B_2O_3 in the single bond strength. That is, the chemical bonding nature of Zn–O bonds is more covalent compared with Bi–O bonds.

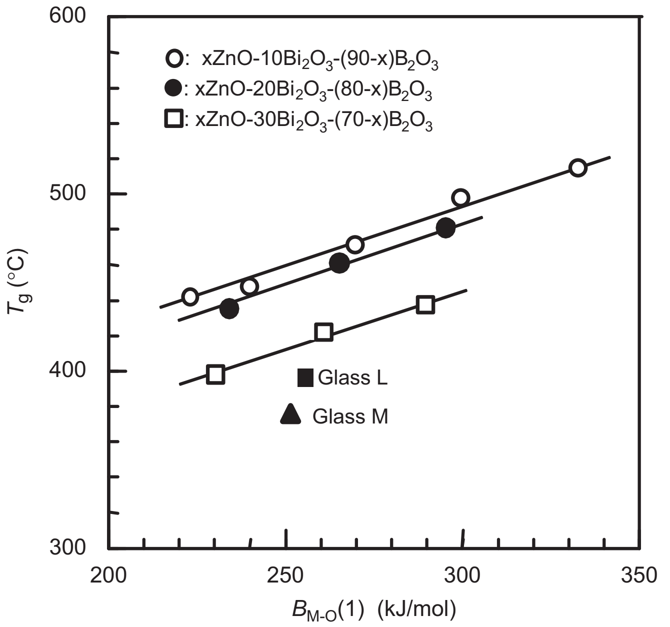

Fig. 11. Correlation between glass transition temperature T_g and average single bond strength B_{M-O} in $ZnO-Bi_2O_3-B_2O_3$ glasses.

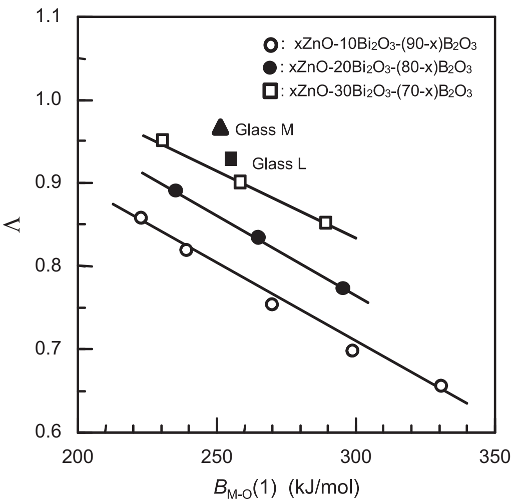

Fig. 12. Correlation between optical basicity Λ and average single bond strength B_{M-O} in $ZnO–Bi_2O_3–B_2O_3$ glasses.

We estimated the packing density, V_p, of constituent ions (Zn^{2+}, Bi^{3+}, B^{3+}, and O^{2-}) for $ZnO–Bi_2O_3–B_2O_3$ glasses from the following equation:

$$V_p = \frac{V_{cal}}{V_m} \qquad (6)$$

where V_m is the molar volume estimated from the density experimentally and V_{cal} is the volume occupied by constituent ions for a given glass composition by considering their ionic radius

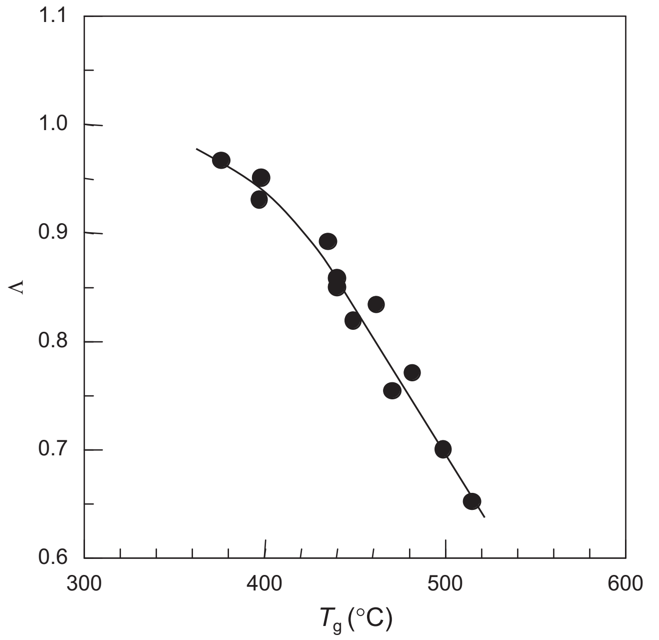

Fig. 13. Correlation between optical basicity Λ and glass transition temperature T_g in $ZnO–Bi_2O_3–B_2O_3$ glasses.

(r) and coordination numbers (CN). The values of $r=0.103$ nm for six CN bismuth, $r=0.06$ nm for four CN zinc, and $r=0.135$ nm for O^{2-} ions were used [39]. For B^{3+} ions, the value of $r=0.0213$ nm was used from the estimation of 70% BO_3 ($r=0.021$ nm for three CN boron) and 30% BO_4 units ($r=0.022$ nm for four CN boron) [39]. The values of V_p obtained are given in Table 1. It is seen that $ZnO–Bi_2O_3–B_2O_3$ glasses have the values of $V_p=0.522–0.578$, which are typical values in oxide glasses [40]. For instance, $40ZnO–10Bi_2O_3–50B_2O_3$ and $60Zn–10Bi_2O_3–30B_2O_3$ glasses show the values of $V_p=0.574$ and 0.534, respectively. As can be seen in Table 1, the substitution of ZnO for B_2O_3 tends to give small packing densities. That is, ZnO creates more open glass network structure in $ZnO–Bi_2O_3–B_2O_3$ glasses. This feature of ZnO might be one reason for the lowering of melting temperatures in $ZnO–B_2O_3$ based glasses.

A good correlation in both T_g vs. $B_{M–O}$ and Λ and $B_{M–O}$ shown in Figs. 11 and 12 suggests another correlation between the glass transition temperature and optical basicity in $ZnO–Bi_2O_3–B_2O_3$ glasses. The values of Λ are plotted as a function of T_g in Fig. 13. It is seen that the optical basicity decreases with increasing the glass transition temperature, and a good correlation is observed. This result suggests that not only the coordination and bonding states of B^{3+} ions (certainly network-former) but also those of Zn^{2+} and Bi^{3+} ions affect strongly the glass transition temperature of $ZnO–Bi_2O_3–B_2O_3$ glasses. Furthermore, a good correlation between T_g and Λ demonstrates again that the average single bond strength is a good parameter for understanding thermal and optical properties of $ZnO–Bi_2O_3–B_2O_3$ glasses.

4. Conclusions

The glasses with the compositions of $xZnO–yBi_2O_3–zB_2O_3$ ($x=10–65$, $y=10–50$, $z=25–60$ mol%) were prepared using a conventional melt quenching method, and the glass transition temperature (T_g), density, refractive index, Raman scattering spectra, and X-ray photoelectron spectra (XPS) were measured to clarify the bonding and structure features of the glasses. It was found that the optical basicity (Λ) of the glasses estimated using Lorentz–Lorenz equation increases with increasing ZnO or Bi_2O_3 content, for example, giving the value of $\Lambda=0.819$ for $60ZnO–10Bi_2O_3–30B_2O_3$ glass. It was suggested from Raman and XPS spectra that B–O–Bi and B–O–Zn bridging bonds are formed in the glass structure. The average single bond strength ($B_{M–O}$) proposed by Dimitrov and Komatsu [6] was applied to the glasses and was calculated using single bond strengths of 150.6 kJ/mol for Zn–O bonds in ZnO_4 groups, 102.5 kJ/mol for Bi–O bonds in BiO_6 groups, 498 kJ/mol for B–O bonds in BO_3 groups, and 373 kJ/mol for B–O bonds in BO_4 groups. The good correlations were observed between T_g and B_{M-O} and Λ and B_{M-O}. The present study proposes that the average single bond strength is a good parameter for understanding thermal and optical properties of $ZnO-Bi_2O_3-B_2O_3$ glasses.

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