FULL PAPER

Correlation between thermal expansion coefficient and interionic interaction parameter in ZnO–Bi₂O₃–B₂O₃ glassesTakayuki KOMATSU^{1,†}, Taisuke INOUE¹, Tina TASHEVA², Tsuyoshi HONMA¹ and Vesselin DIMITROV²¹Department of Materials Science and Technology, Nagaoka University of Technology,
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The volume thermal expansion coefficients (β) in 50–300°C of $x\text{ZnO}-y\text{Bi}_2\text{O}_3-z\text{B}_2\text{O}_3$ glasses ($x = 10-65$, $y = 10-50$, $z = 25-60$ mol %) were measured and the refractive index-based interionic interaction parameters $A(n_o)$ were estimated from oxide ion electronic polarizabilities to acquire deeper insight into the relationship between the electronic polarizability and chemical bonding state of oxide glasses. The glasses have relatively large values of $\beta = 210-289 \times 10^{-7} \text{ K}^{-1}$, and the substitution of ZnO for B₂O₃ and the increase in Bi₂O₃ content result in an increase in β . The values of $A(n_o)$ decrease with the substitution of ZnO for B₂O₃ and the substitution of Bi₂O₃ for ZnO. An almost linear correlation was observed between β and $A(n_o)$, i.e., the volume thermal expansion coefficient decreases with increases in the interionic interaction parameter. A good correlation was also observed between $A(n_o)$ and the refractive index-based optical basicity $\Lambda(n_o)$. The interionic interaction parameter is helpful for understanding the chemical bonding state of oxide glasses.

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1. Introduction

One of the most important properties of materials, which is closely related to their applicability in the field of optics and electronics, is electronic polarizability. After the pioneering work by Duffy and Ingram,^{1,2)} many studies in approaches to the electronic polarizability of glasses and materials have been reported so far. Dimitrov and Komatsu^{3)–7)} proposed the classification (characterization) concept for oxide glasses and materials, for instance, based on the degree of electronic polarizability and explored the electronic polarizability of glasses more deeply from perspective of the interionic interaction parameter of cation and anion (oxygen) pairs and the average single bond strength of constituent oxides in glasses. It is extremely important to evaluate the electronic polarizability and interionic interaction parameters of glasses and also to understand the correlation between the electronic polarizability/interionic interaction parameters and structure/properties of various glasses for development of new functional glasses.

Since the first report by Dumbaugh⁸⁾ on Bi₂O₃-based glasses, numerous studies on Bi₂O₃-based glasses have been conducted so far. It is widely recognized today that Bi₂O₃ oxide is one of the most important constituents for the design and control of optical, electrical, and thermal properties of oxide glasses.⁹⁾ The attractive features of Bi₂O₃ oxide include the large electronic polarizability and weak single bond strength of Bi–O bonds.^{10)–14)} Indeed, glasses with high Bi₂O₃ contents exhibit large third-order nonlinear optical susceptibilities $\chi^{(3)}$ on the order 10^{-12} esu.^{15)–17)} Recently, ZnO–Bi₂O₃–B₂O₃ glasses have received much attention,^{9),18)–22)} in particular, because they are thermally stable low-melting glasses and have been used as new sealing glasses instead of PbO-containing low melting glasses. The crystallization behavior of ZnO–Bi₂O₃–B₂O₃ glasses has also received considerable attention.²³⁾ Very recently, for example, nonlinear optical Bi₂ZnB₂O₇ crystal lines with a high orientation were patterned at the surface of 3Sm₂O₃–33.3ZnO–30.3Bi₂O₃–33.3B₂O₃ glass using a laser-induced crystallization technique,²⁴⁾ thus proposing further new potential for optical device applications of Bi₂O₃-based glasses. It is, therefore, of interest and importance to gain a deeper understanding of the electronic polarizability/interionic interaction parameters and thermal properties of ZnO–Bi₂O₃–B₂O₃ glasses.

In this study, we focus on the thermal expansion

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coefficient and interionic interaction parameters of ZnO–Bi₂O₃–B₂O₃ glasses, especially on their correlation. There has thus far been no report on these topics for ZnO–Bi₂O₃–B₂O₃ glasses. The thermal expansion coefficient is an important property for applications of materials that is closely related to the chemical bond strength and anharmonic oscillation of constituent ions. The present authors proposed in the previous paper²⁰⁾ that there is a good correlation between the electronic polarizability and average single bond strength in ZnO–Bi₂O₃–B₂O₃ glasses. Now, in the present study, we will provide deeper insight into the relationship between the electronic polarizability and chemical bonding state in ZnO–Bi₂O₃–B₂O₃ glasses.

2. Experimental

The chemical compositions of the glasses prepared in the present study were $x\text{ZnO}-y\text{Bi}_2\text{O}_3-z\text{B}_2\text{O}_3$ ($x = 10-65$, $y = 10-50$, $z = 25-60$ mol %). The glasses were prepared using a conventional melt-quenching technique. Commercial powders of reagent grade ZnO, Bi₂O₃, and H₃BO₃ 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. The glass transition temperatures (T_g) were determined using differential thermal analyses at a heating rate of 10 K/min. The quenched glasses were annealed at the temperatures of $T_g-30^\circ\text{C}$ for 1 h to release internal stresses. The densities (d) of the glasses at room temperature were determined by the Archimedes method using distilled water as an immersion liquid. Refractive indices (n_o) at a wavelength of $\lambda = 632.8$ nm (He–Ne laser) were measured at room temperature with a prism coupler (Metricon Model 2010). Linear thermal expansion coefficients α between 50 and 300°C of ZnO–Bi₂O₃–B₂O₃ glasses were measured with rod-shaped samples (length: 10 mm) at a heating rate of 5 K/min in air using a thermomechanical analyzer (Rigaku: TMA8311 Thermo plus EV02). The volume thermal expansion coefficients β were estimated by multiplying α by 3 times.

3. Results and discussion

3.1 Thermal expansion coefficient

The melt-quenched samples for the compositions examined in this study are optically transparent. The amorphous state of the as-quenched samples was confirmed from X-ray diffraction patterns. In the previous paper,²⁰⁾ the present authors' group reported the values of the glass transition temperature, density and refractive index at room temperature for the glasses, and those values are summarized again in **Table 1**. The values of the volume thermal expansion coefficients β obtained in this study are added in Table 1. The values of β in $x\text{ZnO}-10\text{Bi}_2\text{O}_3-(90-x)\text{B}_2\text{O}_3$, $x\text{ZnO}-20\text{Bi}_2\text{O}_3-(80-x)\text{B}_2\text{O}_3$, and $x\text{ZnO}-30\text{Bi}_2\text{O}_3-(70-x)\text{B}_2\text{O}_3$ glasses are plotted as a function of ZnO content in **Fig. 1**. These glasses have relatively large values of $\beta = 210-289 \times 10^{-7} \text{ K}^{-1}$, suggesting a weak chemical bond strength in ZnO–Bi₂O₃–B₂O₃ glasses. As seen in

Table 1. Glass composition, glass transition temperature T_g , density d , refractive index at 632.8 nm n_o , and volume thermal expansion coefficient β for ZnO–Bi₂O₃–B₂O₃ glasses. The values for T_g , d , and n_o are taken from Ref. 20

Sample	Composition (mol %)			T_g (°C)	d (g/cm ³)	n_o	β (K ⁻¹)
	ZnO	Bi ₂ O ₃	B ₂ O ₃				
Glass A	30	10	60	515	4.209	1.748	210×10^{-7}
Glass B	40	10	50	499	4.529	1.784	221×10^{-7}
Glass C	50	10	40	471	4.842	1.815	225×10^{-7}
Glass D	60	10	30	449	5.152	1.851	240×10^{-7}
Glass E	65	10	25	440	5.292	1.870	—
Glass F	30	20	50	482	5.445	1.895	251×10^{-7}
Glass G	40	20	40	462	5.688	1.933	260×10^{-7}
Glass H	50	20	30	435	5.964	1.968	273×10^{-7}
Glass I	20	30	50	440	5.993	1.986	264×10^{-7}
Glass J	30	30	40	421	6.192	2.021	281×10^{-7}
Glass K	40	30	30	398	6.497	2.059	289×10^{-7}
Glass L	20	40	40	397	6.798	2.095	—
Glass M	10	50	40	376	7.151	2.155	—

Fig. 1. Values of the volume thermal expansion coefficient β as a function of ZnO content in ZnO–Bi₂O₃–B₂O₃ glasses. The lines are drawn to guide the eye.

Fig. 1, the substitution of ZnO for B₂O₃ results in an increase in the thermal expansion coefficient. It is found, moreover, that the thermal expansion coefficient increases with increase in Bi₂O₃ content. The following values for single bond strength $B_{\text{M-O}}$ of ZnO, Bi₂O₃, and B₂O₃ simple oxides have been proposed:^{20),25)} $B_{\text{Zn-O}} = 150.6$ kJ/mol for ZnO₄ structural units, $B_{\text{Bi-O}} = 102.5$ kJ/mol for BiO₆ structural units, $B_{\text{B-O}} = 498$ kJ/mol for BO₃ structural units, and $B_{\text{B-O}} = 373$ kJ/mol for BO₄ structural units. The compositional dependence (trend) of β in ZnO–Bi₂O₃–B₂O₃ glasses shown in Fig. 1 is, therefore, explained from the perspective of single bond strength. The volume thermal expansion coefficients of $x\text{Bi}_2\text{O}_3-(100-x)\text{B}_2\text{O}_3$ glasses have been reported, and, for example, the glass with a composition of 32.5Bi₂O₃–67.5B₂O₃ exhibits a

Table 2. Refractive index-based optical basicity $\Lambda(n_o)$, theoretical optical basicity Λ_{th} , refractive index-based interionic interaction parameter $A(n_o)$, theoretical interionic interaction parameter A_{th} , average single bond strength B_{M-O} , mean O1s binding energy E_b , and third-order optical susceptibility $\chi^{(3)}$ calculated using Miller's rule for ZnO–Bi₂O₃–B₂O₃ glasses. The values of B_{M-O} and mean O1s binding energy are taken from Ref. 20

Glass	$\Lambda(n_o)$	Λ_{th}	$A(n_o)$ ($\text{\AA}^{-3}$)	A_{th} ($\text{\AA}^{-3}$)	B_{M-O} (kJ/mol)	E_b (eV)	$\chi^{(3)}$ (esu)
Glass A	0.652	0.600	0.159	0.189	331	531.32	7.2×10^{-14}
Glass B	0.700	0.643	0.143	0.175	300	530.83	9.1×10^{-14}
Glass C	0.754	0.694	0.126	0.158	270	530.87	11.1×10^{-14}
Glass D	0.819	0.757	0.107	0.137	239	530.56	13.9×10^{-14}
Glass E	0.858	0.794	0.096	0.124	223	530.53	15.6×10^{-14}
Glass F	0.771	0.695	0.117	0.160	294		18.1×10^{-14}
Glass G	0.834	0.746	0.099	0.143	265		22.5×10^{-14}
Glass H	0.892	0.808	0.083	0.122	237		27.4×10^{-14}
Glass I	0.850	0.739	0.092	0.147	288		30.2×10^{-14}
Glass J	0.906	0.790	0.077	0.130	259		36.4×10^{-14}
Glass K	0.951	0.850	0.065	0.110	231		44.3×10^{-14}
Glass L	0.931	0.827	0.068	0.119	255		53.0×10^{-14}
Glass M	0.967	0.859	0.058	0.110	250		70.9×10^{-14}

value of $\beta = 175 \times 10^{-7} \text{K}^{-1}$.¹³⁾ As seen in Table 1, 20ZnO–30Bi₂O₃–50B₂O₃ glass has a value of $\beta = 264 \times 10^{-7} \text{K}^{-1}$, indicating that the substitution of ZnO for B₂O₃ results in an increase in the thermal expansion coefficient. This behavior might also be explained from the difference in the single bond strength of ZnO and B₂O₃. Thermal expansion in materials arises from an asymmetric shape of a potential curve in a given material, i.e., anharmonic lattice vibrations. As a general trend, thermal expansion in materials with a shallow potential curve, weak chemical bonds, and a low melting temperature becomes enlarged. The value and compositional dependence of β shown in Fig. 1 reveal good consistency with the characteristic of low-melting Bi₂O₃-based glasses.

3.2 Electronic polarizability and interaction parameter

The electronic polarizabilities and optical basicities of ZnO–Bi₂O₃–B₂O₃ glasses were estimated using the following equations:^{2),5),11),26)}

$$R_m = \left[\frac{(n_o^2 - 1)}{(n_o^2 + 2)} \right] \left(\frac{M}{d} \right) = \left[\frac{(n_o^2 - 1)}{(n_o^2 + 2)} \right] V_m$$

$$= \frac{4\pi\alpha_m N}{3} \quad (1)$$

$$\alpha_{O^{2-}}(n_o) = [\alpha_m - \Sigma\alpha_i](N_{O^{2-}})^{-1} \quad (2)$$

$$\Lambda(n_o) = 1.67 \left[1 - \frac{1}{\alpha_{O^{2-}}(n_o)} \right] \quad (3)$$

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, $\alpha_{O^{2-}}(n_o)$ is the average electronic polarizability of oxide ions, $\Sigma\alpha_i$ denotes molar cation polarizability, $N_{O^{2-}}$ denotes the number of oxide ions in the chemical formula, and Λ is the so-called optical basicity of the oxide medium. Equation (1) is the so-called Lorentz–Lorenz equation giving the relationship between molar refraction (R_m) and refractive index (n_o). Equation (2) proposed by Dimitrov and Sakka²⁶⁾ gives the electronic polarizability of oxide ions

$[\alpha_{O^{2-}}(n_o)]$ in oxide materials by subtracting the cation polarizability ($\Sigma\alpha_i$) from the molar polarizability (α_m). Equation (3) proposed by Duffy²⁾ gives the intrinsic relationship between the electronic polarizability of the oxide ions and the so-called optical basicity of the oxide medium $[\Lambda(n_o)]$. The optical basicity of an oxide medium as proposed by Duffy and Ingram^{1),27)} is a numerical expression of the average electron donor power of the oxide species constituting the medium. Because increased oxide ion polarizability means a stronger electron donor ability of the oxide ions, the physical background of the oxide ion polarizability and optical basicity is naturally the same. The values of α_m , $\alpha_{O^{2-}}(n_o)$ and $\Lambda(n_o)$ of ZnO–Bi₂O₃–B₂O₃ glasses were estimated using Eqs. (1)–(3) in the previous paper,²⁰⁾ and the results for $\Lambda(n_o)$ are summarized again in **Table 2**.

The refractive index-based interionic interaction parameters $A(n_o)$ (unit: $\text{\AA}^{-3}$) of ZnO–Bi₂O₃–B₂O₃ glasses were estimated using the following Eq. (4) for the first time in this study:^{4),5),7),10),11)}

$$A(n_o) = X_{ZnO} \frac{[\alpha_f^- - \alpha_{O^{2-}}(n_o)]}{2(\alpha_{Zn^{2+}} + \alpha_f^-)[\alpha_{Zn^{2+}} + \alpha_{O^{2-}}(n_o)]}$$

$$+ X_{Bi_2O_3} \frac{[\alpha_f^- - \alpha_{O^{2-}}(n_o)]}{2(\alpha_{Bi^{3+}} + \alpha_f^-)[\alpha_{Bi^{3+}} + \alpha_{O^{2-}}(n_o)]}$$

$$+ X_{B_2O_3} \frac{[\alpha_f^- - \alpha_{O^{2-}}(n_o)]}{2(\alpha_{B^{3+}} + \alpha_f^-)[\alpha_{B^{3+}} + \alpha_{O^{2-}}(n_o)]} \quad (4)$$

In Eq. (4), α_f^- ($\text{\AA}^3$) is the electronic polarizability of the free oxide ion, and the ionic refraction of O^{2-} theoretically determined by Pauling²⁸⁾ was used as the value of α_f^- , i.e., $\alpha_f^- = 3.921 \text{\AA}^3$. The values of $\alpha_{Zn^{2+}} = 0.283 \text{\AA}^3$, $\alpha_{Bi^{3+}} = 1.508 \text{\AA}^3$, and $\alpha_{B^{3+}} = 0.002 \text{\AA}^3$ are used as the electronic polarizability of Zn^{2+} , Bi^{3+} , and B^{3+} ions in the free state, respectively. The data for cation polarizabilities are taken from Ref. 26. X_{ZnO} , $X_{Bi_2O_3}$, and $X_{B_2O_3}$ are the equivalent fractions of ZnO, Bi₂O₃, and B₂O₃ based on the amount of oxygen, respectively. The values of $A(n_o)$ estimated in the present study for ZnO–Bi₂O₃–B₂O₃ glasses are summarized in Table 2.

Fig. 2. Values of the interionic interaction parameter $A(n_o)$ as a function of ZnO content in ZnO-Bi₂O₃-B₂O₃ glasses. The lines are drawn to guide the eye.

The values of $A(n_o)$ in $x\text{ZnO}-10\text{Bi}_2\text{O}_3-(90-x)\text{B}_2\text{O}_3$, $x\text{ZnO}-20\text{Bi}_2\text{O}_3-(80-x)\text{B}_2\text{O}_3$, and $x\text{ZnO}-30\text{Bi}_2\text{O}_3-(70-x)\text{B}_2\text{O}_3$ glasses are plotted as a function of ZnO content in Fig. 2. It is seen that the interionic interaction parameter decreases with the substitution of ZnO for B₂O₃. The values of $A(n_o)$ in $(50-y)\text{ZnO}-y\text{Bi}_2\text{O}_3-50\text{B}_2\text{O}_3$, $(60-y)\text{ZnO}-y\text{Bi}_2\text{O}_3-40\text{B}_2\text{O}_3$, and $(70-y)\text{ZnO}-y\text{Bi}_2\text{O}_3-30\text{B}_2\text{O}_3$ glasses are plotted as a function of Bi₂O₃ content in Fig. 3. It is found that the interionic interaction parameter decreases with the substitution of Bi₂O₃ for ZnO. The interionic interaction parameter, which was proposed for ionic crystals by Yamashita and Kurosawa²⁹⁾ and applied to simple oxide and glasses by Dimitrov and Komatsu,^{4),30)} represents the charge overlapping of a negative ion such as O²⁻ with its nearest positive ion such as B³⁺. In other words, the interionic interaction parameter in oxides means interionic interaction between cations and average oxide ions due to overlapping of their outermost electronic orbitals to form chemical bonds. Thus, oxides with strong chemical bonds tend to have large interionic interaction parameters. As reported by Dimitrov and Komatsu,¹¹⁾ the interionic interaction parameter of simple oxides is $A = 0.244 \text{ \AA}^{-3}$ for B₂O₃, $A = 0.040 \text{ \AA}^{-3}$ for ZnO, and $A = 0.008 \text{ \AA}^{-3}$ for Bi₂O₃, indicating that the order of chemical bond strength between O²⁻ and cations is B₂O₃ > ZnO > Bi₂O₃. The compositional dependence of $A(n_o)$ in ZnO-Bi₂O₃-B₂O₃ glasses shown in Figs. 2 and 3 is, therefore, well explained by the difference in the chemical bond strength of ZnO, Bi₂O₃, and B₂O₃ oxides. It has been established that the interionic interaction parameter is closely related to oxide ion polarizability and thus to optical basicity.^{4),30)} That is, oxides with a large inter-

Fig. 3. Values of the interionic interaction parameter $A(n_o)$ as a function of Bi₂O₃ content in ZnO-Bi₂O₃-B₂O₃ glasses. The lines are drawn to guide the eye.

Fig. 4. Correlation between the interionic interaction parameter $A(n_o)$ and the optical basicity $\Lambda(n_o)$ in ZnO-Bi₂O₃-B₂O₃ glasses. The line is drawn to guide the eye.

ionic interaction parameter tend to have small optical basicity. The values for $\Lambda(n_o)$ in ZnO-Bi₂O₃-B₂O₃ glasses are plotted as a function of $A(n_o)$ in Fig. 4. The optical basicity decreases with increases in the interionic interaction parameter and a good correlation is observed between these two parameters, demonstrating the presence of a close correlation even in low-melting ZnO-Bi₂O₃-B₂O₃ glasses. The values for d , n_o , $\Lambda(n_o)$, and β reported in the previous study²⁰⁾ for the binary Bi₂O₃-B₂O₃ glasses are summarized in Table 3 for comparison.

Table 3. Glass composition, density d , refractive index at 632.8 nm n_o , refractive index-based optical basicity $\Lambda(n_o)$, theoretical optical basicity Λ_{th} , refractive index-based interionic interaction parameter $A(n_o)$, theoretical interionic interaction parameter A_{th} , volume thermal expansion coefficient β , and third-order optical susceptibilities $\chi^{(3)}$ for $y\text{Bi}_2\text{O}_3-(100-y)\text{B}_2\text{O}_3$ glasses. The values for d , n_o , $\Lambda(n_o)$, and β are taken from Ref. 20 and the values for $\chi^{(3)}$ are taken from Ref. 17

y (mol %)	d (g/cm ³)	n_o	$\Lambda(n_o)$	Λ_{th}	$A(n_o)$ (Å ⁻³)	A_{th} (Å ⁻³)	β (K ⁻¹)	$\chi^{(3)}$ (esu)
32.5	5.584	1.931	0.796	0.677	0.108	0.167	175×10^{-7}	
40	6.254	2.009	0.845	0.734	0.091	0.150	188×10^{-7}	51.5×10^{-14}
50	6.824	2.112	0.937	0.810	0.066	0.126	212×10^{-7}	63.4×10^{-14}
60	7.457	2.218	0.998	0.886	0.050	0.102	232×10^{-7}	81.3×10^{-14}

Fig. 5. Correlation between the volume thermal expansion coefficient β and the interionic interaction parameter $A(n_o)$ in ZnO–Bi₂O₃–B₂O₃ glasses. The line is drawn to guide the eye.

3.3 Correlation between thermal expansion coefficient and interionic interaction parameter

The values of β in ZnO–Bi₂O₃–B₂O₃ glasses are plotted as a function of $A(n_o)$ in **Fig. 5**. It is seen that the volume thermal expansion coefficient decreases with increases in the interionic interaction parameter. A good correlation, i.e., almost a linear correlation, is clearly observed between them, moreover, suggesting that the interionic interaction parameter is a good indicator for the thermal expansion coefficient and also demonstrating that the main factor for the thermal expansion coefficient in ZnO–Bi₂O₃–B₂O₃ glasses is the chemical bond strength between O²⁻ ions and cations of Zn²⁺, Bi³⁺, and B³⁺. The values of T_g in ZnO–Bi₂O₃–B₂O₃ glasses are plotted as a function of $A(n_o)$ in **Fig. 6**. The glass transition temperature increases with increases in the interionic interaction parameter. The glass transition temperature is closely related to the primary structural relaxation in the transition from the solid glassy state to the viscous super-cooled liquid state, i.e., the so-called α -relaxation and atomic rearrangements in the glass network structure. The results shown in **Fig. 6** suggest that the chemical bond strength between the O²⁻

Fig. 6. Correlation between the glass transition temperature T_g and the interionic interaction parameter $A(n_o)$ in ZnO–Bi₂O₃–B₂O₃ glasses. The lines are drawn to guide the eye.

ions and cations of Zn²⁺, Bi³⁺, and B³⁺ is one of the main factors determining the glass transition temperature in the ternary ZnO–Bi₂O₃–B₂O₃ glasses.

In the previous paper,²⁰⁾ the structure of ZnO–Bi₂O₃–B₂O₃ glasses was examined based on Raman scattering spectra and X-ray photoelectron spectra (XPS), and the formation of B–O–Bi and B–O–Zn bridging bonds was suggested and the mean O1s binding energy obtained. The concept of average single bond strength (B_{M-O}) proposed by Dimitrov and Komatsu³¹⁾ was applied to ZnO–Bi₂O₃–B₂O₃ glasses, moreover, and the values of B_{M-O} were evaluated based on structural units, e.g., the fractions of BO₃ and BO₄ units. The values reported for B_{M-O} and the mean O1s binding energy are summarized in Table 2. The values of the interaction parameter $A(n_o)$ in ZnO–Bi₂O₃–B₂O₃ glasses are plotted as a function of B_{M-O} and the mean O1s binding energy in **Figs. 7** and **8**, respectively. It is seen that the interionic interaction parameter increases with increases in B_{M-O} and the mean O1s binding energy, demonstrating again usefulness of the interionic interaction parameter for understanding the chemical bonding state of ZnO–Bi₂O₃–B₂O₃ glasses.

The most widely quoted model to describe the temper-

Fig. 7. Correlation between the interionic interaction parameter $A(n_0)$ and the average single bond strength B_{M-O} in ZnO-Bi₂O₃-B₂O₃ glasses. The lines are drawn to guide the eye.

Fig. 8. Correlation between the interionic interaction parameter $A(n_0)$ and the mean O1s binding energy in ZnO-Bi₂O₃-B₂O₃ glasses. The line is drawn to guide the eye.

ature dependence of the refractive index of glasses dn/dT is that of Prod'homme,³²⁾ in which two counteracting factors have been considered, i.e., thermal expansion and electronic polarizability. Prod'homme³²⁾ proposed the following equation by differentiating the Lorentz-Lorenz equation:

$$\frac{dn}{dT} = \frac{(n^2 - 1)(n^2 + 2)}{6n} (\phi - \beta) \quad (5)$$

where β is the volume thermal expansion coefficient and ϕ is the polarizability coefficient defined as the temperature dependence of electronic polarizability. Equation (5) is, therefore, regarded as an expression of the relationship

Fig. 9. Correlation between the interionic interaction parameter $A(n_0)$ and third-order optical susceptibility $\chi^{(3)}$ estimated from Miller's rule in ZnO-Bi₂O₃-B₂O₃ glasses (○). The values for Bi₂O₃-B₂O₃ glasses (●) are taken from Ref. 17. The line is drawn to guide the eye.

between electronic polarizability and the thermal expansion coefficient, i.e., the relationship between $A(n_0)$ and β . Komatsu et al.¹³⁾ measured the temperature dependence of the refractive index in the temperature range of 30–150°C in Bi₂O₃-B₂O₃ glasses and found that it increases with increases in Bi₂O₃ content. They found, moreover, that the temperature dependences of the refractive index for the Bi₂O₃-B₂O₃ glasses are much larger compared with other glasses of Na₂O-Al₂O₃-SiO₂ and Na₂O-B₂O₃ as well as with commercial optical glasses. This behavior is clearly related to the large electronic polarizability of oxide ions in Bi₂O₃. Even in ZnO-Bi₂O₃-B₂O₃ glasses, the fact that Bi₂O₃ has a large electronic polarizability and weak single bond strength contributes largely to the thermal expansion coefficient of the glasses.

It is well known that Bi₂O₃-based glasses exhibit large third-order optical susceptibilities $\chi^{(3)}$.^{15)–17)} It is of interest to estimate the values of $\chi^{(3)}$ (esu) for ZnO-Bi₂O₃-B₂O₃ glasses. In this paper, we calculated $\chi^{(3)}$ using the so-called Miller's rule:^{33),34)}

$$\chi^{(3)} = \left(\frac{n^2 - 1}{4\pi} \right)^4 \times 10^{-10} \quad [\text{esu}] \quad (6)$$

The estimated values of $\chi^{(3)}$ are summarized in Table 2 and also plotted as a function of the interionic interaction parameter $A(n_0)$ in Fig. 9. Glasses with Bi₂O₃ contents of 30, 40, and 50 mol % are expected to have values of $\chi^{(3)} = 3\text{--}7 \times 10^{-13}$ esu. As seen in Fig. 9, moreover, a good correlation is expected between the third-order optical susceptibility and interionic interaction parameter. The values of $\chi^{(3)}$ for some Bi₂O₃-B₂O₃ glasses reported by Terashima et al.¹⁷⁾ are also summarized in Table 3. It is expected that ternary ZnO-Bi₂O₃-B₂O₃ glasses have a potential for optical device applications similar to that of binary Bi₂O₃-B₂O₃ glasses.

Fig. 10. Correlation between the experimentally determined interionic interaction parameter $A(n_o)$ and the theoretically calculated interionic interaction parameter A_{th} in ZnO–Bi₂O₃–B₂O₃ and Bi₂O₃–B₂O₃ glasses.

3.4 Theoretical interionic interaction parameter

The so-called theoretical optical basicity Λ_{th} , which is based on the approach by Duffy and Haris,³⁵⁾ and the theoretical interionic interaction parameter A_{th} , which was first introduced by Dimitrov and Komatsu,³⁰⁾ are very important concepts for deep understanding of the electronic polarizability and chemical bonding strength of materials. In the case of multi-component glasses, it is possible to determine the values of the optical basicity and interionic interaction parameter from their chemical compositions without measuring the density and refractive index of a given glass. Considered from this perspective, it is of interest and importance to compare the values of $\Lambda(n_o)$ and $A(n_o)$ determined from the measured density and refractive index with the theoretical values. The values of Λ_{th} and A_{th} in the ternary ZnO–Bi₂O₃–B₂O₃ glasses are calculated using the following equations:

$$\Lambda_{th} = X_{ZnO}\Lambda_{ZnO} + X_{Bi_2O_3}\Lambda_{Bi_2O_3} + X_{B_2O_3}\Lambda_{B_2O_3} \quad (7)$$

$$A_{th} = X_{ZnO}A_{ZnO} + X_{Bi_2O_3}A_{Bi_2O_3} + X_{B_2O_3}A_{B_2O_3} \quad (8)$$

In Eqs. (7) and (8), Λ_{ZnO} , $\Lambda_{Bi_2O_3}$, and $\Lambda_{B_2O_3}$ are the optical basicities of simple oxides of ZnO, Bi₂O₃, and B₂O₃, respectively, and A_{ZnO} , $A_{Bi_2O_3}$, and $A_{B_2O_3}$ are the interionic interaction parameters of simple oxides. In the calculation, the following values were used:^{5),11),26)} $\Lambda_{ZnO} = 1.03$, $\Lambda_{Bi_2O_3} = 1.19$, $\Lambda_{B_2O_3} = 0.43$, $A_{ZnO} = 0.040 \text{ Å}^{-3}$, $A_{Bi_2O_3} = 0.008 \text{ Å}^{-3}$, and $A_{B_2O_3} = 0.244 \text{ Å}^{-3}$. The theoretically calculated values for Λ_{th} and A_{th} of ZnO–Bi₂O₃–B₂O₃ glasses are summarized in Table 2. The correlation between the experimentally determined values and theoretically calculated values is shown in Fig. 10 for the interionic interaction parameter and in Fig. 11 for the optical basicity. In these figures, the values obtained for the binary Bi₂O₃–

Fig. 11. Correlation between the experimentally determined optical basicity $\Lambda(n_o)$ and the theoretically calculated optical basicity Λ_{th} in ZnO–Bi₂O₃–B₂O₃ and Bi₂O₃–B₂O₃ glasses.

B₂O₃ glasses (Table 3) are also plotted. A good correlation is observed for both parameters, although there is a deviation in the values.

The values of the interionic interaction parameters of simple oxides such as A_{ZnO} , $A_{Bi_2O_3}$, and $A_{B_2O_3}$ have been evaluated based on the values of the density and refractive index of simple crystalline oxides. As a first approximation, it is assumed that the electronic polarizability of oxide ions and cations and also the chemical bonding strength between oxide ions and cations in oxide glasses would be close to those in oxide crystals. This is a basic concept for theoretical interionic interaction parameter and optical basicity expressed by Eqs. (7) and (8). Of course, we know that the coordination state and chemical bonding state of ions in glasses are extremely complicated, e.g., the presence of different oxygen coordination numbers such as BO₃ and BO₄, the presence of bridging and non-bridging oxygens, and a wide distribution of ionic distance and bonding angles. The flexibility and distribution in the structure and bonding in glasses might be one reason for the deviations between the experimentally determined values and theoretically calculated values shown in Figs. 10 and 11. As shown in Tables 2 and 3, the glasses containing high Bi₂O₃ contents tend to show a large deviation between $A(n_o)$ and A_{th} as well as between $\Lambda(n_o)$ and Λ_{th} , suggesting that Bi₂O₃ in ZnO–Bi₂O₃–B₂O₃ and Bi₂O₃–B₂O₃ glasses might have an electronic polarizability larger than that expected in simple crystalline Bi₂O₃ oxide.

4. Conclusion

The volume thermal expansion coefficients (β) in 50–300°C of $x\text{ZnO} \cdot y\text{Bi}_2\text{O}_3 \cdot z\text{B}_2\text{O}_3$ glasses ($x = 10\text{--}65$, $y = 10\text{--}50$, $z = 25\text{--}60 \text{ mol } \%$) were measured and the inter-

ionic interaction parameters $A(n_o)$ were estimated from oxide ion electronic polarizabilities in order to obtain deep insight into the relationship between the electronic polarizability and chemical bonding state of oxide glasses. The glasses showed relatively large values of $\beta = 210\text{--}289 \times 10^{-7} \text{ K}^{-1}$, and the values of β were increased with the substitution of ZnO for B_2O_3 and an increase in Bi_2O_3 content. The values of $A(n_o)$ decreased with the substitution of ZnO for B_2O_3 and the substitution of Bi_2O_3 for ZnO. A nearly linear correlation was observed between β and $A(n_o)$, i.e., the volume thermal expansion coefficient decreases with increases in the interionic interaction parameter, indicating that the interionic interaction parameter is appropriate for understanding the chemical bonding state of the glasses. A good correlation was also observed between $A(n_o)$ and optical basicity $\Lambda(n_o)$.

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References

- 1) J. A. Duffy and M. D. Ingram, *J. Non-Cryst. Solids*, **21**, 373–410 (1976).
- 2) J. A. Duffy, *Phys. Chem. Glasses*, **30**, 1–4 (1989).
- 3) V. Dimitrov and T. Komatsu, *J. Non-Cryst. Solids*, **249**, 160–179 (1999).
- 4) V. Dimitrov and T. Komatsu, *J. Ceram. Soc. Jpn.*, **107**, 1012–1018 (1999).
- 5) V. Dimitrov and T. Komatsu, *J. Solid State Chem.*, **178**, 831–846 (2005).
- 6) V. Dimitrov and T. Komatsu, *J. Solid State Chem.*, **196**, 574–578 (2012).
- 7) V. Dimitrov and T. Komatsu, *J. Univ. Chem. Technol. Metall.*, **45**, 219–250 (2010).
- 8) W. H. Dumbaugh, *Phys. Chem. Glasses*, **27**, 119–123 (1986).
- 9) T. Maeder, *Int. Mater. Rev.*, **58**, 3–40 (2013).
- 10) T. Honma, Y. Benino, T. Komatsu, R. Sato and V. Dimitrov, *Phys. Chem. Glasses*, **43**, 32–40 (2002).
- 11) V. Dimitrov and T. Komatsu, *J. Solid State Chem.*, **163**, 100–112 (2002).
- 12) V. Dimitrov and T. Komatsu, *J. Non-Cryst. Solids*, **356**, 258–262 (2010).
- 13) T. Komatsu, N. Ito, T. Honma and V. Dimitrov, *J. Non-Cryst. Solids*, **356**, 2310–2314 (2010).
- 14) V. Dimitrov and T. Komatsu, *J. Non-Cryst. Solids*, **382**, 18–23 (2013).
- 15) H. Nasu, T. Ito, H. Hase, J. Matsuoka and K. Kamiya, *J. Non-Cryst. Solids*, **204**, 78–82 (1996).
- 16) N. Sugimoto, H. Kanbara, S. Fujiwara, K. Tanaka and K. Hirao, *Opt. Lett.*, **21**, 1637–1639 (1996).
- 17) K. Terashima, T. Shimoto and T. Yoko, *Phys. Chem. Glasses*, **38**, 211–217 (1997).
- 18) D. Saritha, Y. Markandeya, M. Salagram, M. Vithal, A. K. Sihng and G. Bhikshamaiah, *J. Non-Cryst. Solids*, **354**, 5573–5579 (2008).
- 19) S. Bale, S. Rahman, A. M. Awasthi and V. Sathe, *J. Alloy. Compd.*, **460**, 699–703 (2008).
- 20) T. Inoue, T. Honma, V. Dimitrov and T. Komatsu, *J. Solid State Chem.*, **183**, 3078–3085 (2010).
- 21) T. Hashimoto, Y. Shimoda, H. Nasu and A. Ishihara, *J. Am. Ceram. Soc.*, **94**, 2061–2066 (2011).
- 22) H. Ticha, M. Kincl and I. Tichy, *Mater. Chem. Phys.*, **138**, 633–639 (2013).
- 23) K. Kanenishi, S. Sakida, Y. Benino and T. Nanba, *J. Ceram. Soc. Jpn.*, **120**, 509–512 (2012).
- 24) T. Inoue, X. Gao, K. Shinozaki, T. Honma and T. Komatsu, *Front. Mater.: Glass Sci.*, **2**, 42 (2015).
- 25) H. Sun, *J. Am. Ceram. Soc.*, **30**, 277–281 (1947).
- 26) V. Dimitrov and S. Sakka, *J. Appl. Phys.*, **79**, 1736–1740 (1996).
- 27) J. A. Duffy and M. D. Ingram, *J. Am. Chem. Soc.*, **93**, 6448–6454 (1971).
- 28) L. Pauling, *P. Roy. Soc. Lond. A Mat.*, **114**, 181–211 (1927).
- 29) J. Yamashita and T. Kurosawa, *J. Phys. Soc. Jpn.*, **10**, 610–633 (1955).
- 30) V. Dimitrov and T. Komatsu, *J. Ceram. Soc. Jpn.*, **108**, 330–338 (2000).
- 31) V. Dimitrov and T. Komatsu, *Phys. Chem. Glasses*, **46**, 521–529 (2005).
- 32) L. Prod'homme, *Phys. Chem. Glasses*, **1**, 119–122 (1960).
- 33) R. C. Miller, *Appl. Phys. Lett.*, **5**, 17–19 (1964).
- 34) C. C. Wang, *Phys. Rev. B*, **2**, 2045–2048 (1970).
- 35) J. A. Duffy and B. Haris, *Ironmak. Steelmak.*, **22**, 132–136 (1995).