FULL PAPER

Composition dependence of absorption edge energy of borate glasses containing a large amount of Bi_2O_3

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Absorption edge energy has been studied in Bi_2O_3 – B_2O_3 , and $(\text{Li}_2\text{O}, \text{Na}_2\text{O}, \text{K}_2\text{O}, \text{CaO}, \text{BaO}, \text{ZnO}, \text{Ga}_2\text{O}_3$ and $\text{Nb}_2\text{O}_5)$ – Bi_2O_3 – B_2O_3 glasses containing a large amount of Bi_2O_3 . It was found that the absorption edge energy obeyed Duffy's theoretical basicity formula, that is, the additivity rule with glass composition. The additivity factor depended on electronegativity of each constituent atom, except bismuth. The additivity factor of Bi_2O_3 was much smaller than that expected from electronegativity. The small value of additivity factor of Bi_2O_3 was discussed on the basis of Bi–O–Bi bond formation.

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1. Introduction

Bismuth oxide attracts attention as an alternative of lead oxide in glass industry from the view point of environmental issue, since bismuth oxide has low toxicity and the addition of bismuth oxide into glasses lowers glass transition temperature and increases refractive index.^{1)–17)} It is known, however, that addition of a large amount of bismuth oxide colors glasses yellow or yellowish brown. The former and the latter colors are due to bismuth ions and bismuth metallic colloid, respectively.¹⁸⁾ Although the browning, that is, the formation of bismuth colloid, can be avoided by decreasing the melting temperature, the yellowing is the intrinsic nature of bismuth ions and is inevitable.

Bismuth containing borate glasses have been studied and have been developed for the production of lenses by a press forming method.^{15)–17)} As a matter of course, colorless glass is preferable for the use of lenses. Therefore, it is important to study the relationship between the color of bismuth-rich glasses and the glass composition. In a previous study, we studied the compositional dependence of short-wavelength absorption edge energy in various bismuth-rich phosphate glasses in detail.¹²⁾ In bismuth-rich borate glasses, many researches have been conducted on the absorption edge energy.^{1)–4)} It has been reported that the absorption edge energy shifted toward lower energy with increasing Bi_2O_3 content in Bi_2O_3 – B_2O_3 , Li_2O – Bi_2O_3 – B_2O_3 and ZnO – Bi_2O_3 – B_2O_3 .^{1)–3)} However, the relationship

between the absorption edge energy and the composition has not been studied in detail within the bismuth rich borate glasses. In the present study, we have studied the absorption edge energy of bismuth containing borate glasses in the bismuth-rich region and discussed the relationship between the absorption edge energy and the composition.

2. Experimental procedures

Glasses listed in **Table 1** were prepared by a conventional melting method. Glass compositions were chosen by reference to glass forming regions in Ref. 19. Reagent grade Bi_2O_3 (Wako Chemicals, 99.9%), B_2O_3 (Kanto Chemicals, 95.0%), CaCO_3 (Kojundo Chemicals, 99%), BaCO_3 (Kojundo Chemicals, 99.5%), ZnO (High Purity Chemicals, 99.9%), Li_2CO_3 (Kojundo Chemicals, 99%), Na_2CO_3 (Kojundo Chemicals, 99%), K_2CO_3 (Kojundo Chemicals, 99%), Ga_2O_3 (Kisida, 99.999%) and Nb_2O_5 (Wako Chemicals, 99.9%) were used as raw materials. The appropriate mixture of these raw materials was melted in a Pt crucible for 1 h at temperatures from 800 to 900°C by an electrically heating furnace in an ambient atmosphere, except for Nb_2O_5 – Bi_2O_3 – B_2O_3 glasses which were melted at temperatures from 950 to 1050°C. The melt was poured onto a carbon plate and annealed at about glass transition temperature to obtain glass with a weight of 20 g and a thickness of 1–3 mm. The glasses were transparent and were colorless, pale-yellow, yellow or chrome yellow. The glass was cut and polished for the measurements of optical absorption spectra, reflection spectra and refractive index. In addition, a thin $50\text{Bi}_2\text{O}_3$ · $50\text{B}_2\text{O}_3$ glass film was prepared from a glass balloon. The thickness of the thin film was estimated to be about 1.3 μm from the period of

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Table 1. Nominal composition and properties of bismuth borate glasses

Nominal Composition/mol %			n	d g cm ⁻³	T_g °C	E_{edge} eV	E_{ref} eV
B ₂ O ₃	Bi ₂ O ₃	Li ₂ O					
40.0	60.0	—	2.207	7.449	356	2.91	4.05
50.0	50.0	—	2.115	6.883	392	3.07	4.20
60.0	40.0	—	2.014	6.226	427	3.21	4.35
70.0	30.0	—	1.897	5.342	451	3.33	4.52
35.0	55.0	10.0	2.184	7.220	330	2.85	—
30.0	50.0	20.0	2.165	6.964	302	2.72	3.77
25.0	45.0	30.0	2.135	6.684	288	2.71	—
45.0	45.0	10.0	2.089	6.639	361	3.01	4.11
40.0	40.0	20.0	2.062	6.344	335	2.94	3.97
35.0	35.0	30.0	2.025	5.990	308	2.85	—
55.0	35.0	10.0	1.982	5.911	403	3.15	4.32
50.0	30.0	20.0	1.959	5.662	375	3.07	—
45.0	25.0	30.0	1.912	5.189	344	2.96	4.22
65.0	25.0	10.0	1.859	5.010	433	3.28	4.38
60.0	20.0	20.0	1.829	4.661	417	3.21	4.43
55.0	15.0	30.0	1.774	4.202	400	3.17	4.36
75.0	15.0	10.0	1.724	3.939	453	3.42	4.56
70.0	10.0	20.0	1.677	3.485	451	3.39	4.64
B ₂ O ₃	Bi ₂ O ₃	ZnO					
35.0	55.0	10.0	2.204	7.439	354	2.90	3.80
30.0	50.0	20.0	2.197	7.363	349	2.95	3.99
25.0	45.0	30.0	2.190	7.334	348	2.88	3.97
45.0	45.0	10.0	2.108	6.863	393	3.04	4.11
40.0	40.0	20.0	2.096	6.778	390	3.06	4.15
35.0	35.0	30.0	2.083	6.702	387	3.05	4.11
55.0	35.0	10.0	2.004	6.153	433	3.19	4.30
50.0	30.0	20.0	1.986	6.049	430	3.19	4.20
45.0	25.0	30.0	1.957	5.893	428	3.19	4.30
65.0	25.0	10.0	1.882	5.238	461	3.32	4.52
60.0	20.0	20.0	1.856*	5.139	463	3.31	4.51
55.0	15.0	30.0	1.824	4.828	486	3.31	4.43
B ₂ O ₃	Bi ₂ O ₃	Ga ₂ O ₃					
25.0	65.0	10.0	2.255	7.739	348	2.80	3.80
35.0	55.0	10.0	2.171	7.267	374	2.97	4.17
45.0	45.0	10.0	2.080	6.693	409	3.11	4.23
55.0	35.0	10.0	1.979	6.011	442	3.23	4.35
65.0	25.0	10.0	1.865	5.138	472	3.36	4.56
B ₂ O ₃	Bi ₂ O ₃	Nb ₂ O ₅					
57.5	37.5	5.0	2.043	6.116	447	3.16	4.35
55.0	35.0	10.0	2.075*	5.994	456	3.09	—
67.5	27.5	5.0	1.925	5.217	461	3.26	4.46
B ₂ O ₃	Bi ₂ O ₃	Na ₂ O					
55.0	35.0	10.0	1.951	5.881	381	3.09	—
B ₂ O ₃	Bi ₂ O ₃	K ₂ O					
65.8	29.0	5.2	1.862	5.155	425	3.23	—
B ₂ O ₃	Bi ₂ O ₃	CaO					
55.0	35.0	10.0	1.995	6.009	436	3.14	4.26
B ₂ O ₃	Bi ₂ O ₃	BaO					
55.0	35.0	10.0	1.994	6.150	417	3.10	—

n : refractive index, d : density, T_g : glass transition temperature, E_{edge} : absorption edge energy, E_{ref} : peak energy of reflection spectra. The errors in n and d were within 0.002 except the data marked with *: The error marked with * was within 0.004.

interference pattern observed in the transmission spectrum and the refractive index.

Near infrared-visible-ultra violet absorption spectra of all the glasses were measured with a conventional spec-

trophotometer (Hitachi U-4000) in the regions from 190 to 800 nm. Ultraviolet reflection spectra of some glasses were measured with the same spectrometer equipped with the reflection measurement attachment in the region from 200 to 600 nm. The incident and take-off angles were kept at an angle of 10° off normal incidence in the reflection measurement. Refractive index at 632.8 nm was measured by a prism coupling method (Metricon, Model 2010 Prism Coupler). The measurement error was almost always within 0.002. Glass transition temperature was measured with a differential thermal analyzer (Rigaku, Thermo plus TG8120) or a differential scanning calorimeter (SII, EXSTAR 600 DSC 5300). Density was measured by the Archimedes' method. The measurement error was almost always less than 0.002 g cm⁻³.

The absorption coefficient, α , of 50Bi₂O₃·50B₂O₃ glass was calculated from absorbance ($\ln T$; T : total transmittance) and sample thickness, following the subtraction of the effect of reflection at sample surfaces. The effect of reflection was estimated from the reflection spectrum or the difference in transmittance of samples with different thickness.

Molar absorption coefficient of Bi₂O₃, κ , of all the glasses was calculated from absorbance by subtracting the effect of reflection which was assumed to be the absorbance at 800 nm, and by being divided by the sample thickness and the molar concentration of Bi₂O₃. The absorption edge energy, E_{edge} , was defined as the energy at which κ was unity. Specifically, E_{edge} was obtained by fitting the function $\exp[B(E - E_{\text{edge}})]$,²⁰⁾ where B is the slope of exponential function and E is the photon energy, to a κ vs. E curve in the region from 2 to 3 Bi₂O₃ mol⁻¹ dm³ cm⁻¹. The peak energy in the reflection spectra was obtained after smoothing the spectra. The measurement error of the peak energy was about 0.1 eV, since the reflection bands were very broad.

3. Results

Density, refractive index and glass transition temperature are summarized in Table 1. **Figure 1** shows transmission spectra and a reflection spectrum of 50Bi₂O₃·50B₂O₃ glass, along with a transmission spectrum of B₂O₃ glass. No absorption peak was observed up to 3.8 eV in the transmission spectra of 50Bi₂O₃·50B₂O₃ glass. An interference pattern was observed in the sample with a thickness of 1.3 μm. A peak was observed at about 4.0 eV in the reflection spectrum of 50Bi₂O₃·50B₂O₃ glass. No absorption bands were observed at energies lower than 5.5 eV in the spectrum of B₂O₃ glass, although the weak interference with a long period was observed.

Figure 2 shows the molar absorption coefficient and reflection spectra of some representative glasses. The absorption edge shifted toward lower energy with the substitution of Bi₂O₃ for B₂O₃. The absorption edge energies, E_{edge} , are summarized in Table 1. The value of B ranged from 8 to 12. A peak was observed in the region from 3.7 to 4.6 eV in the reflection spectra. The peak energy shifted toward lower energy with the substitution of Bi₂O₃ for

Fig. 1. Transmittance and reflectance of 50Bi₂O₃·50B₂O₃ glass along with transmittance of B₂O₃ glass. Thick solid and dotted lines represent transmittance and reflectance of 50Bi₂O₃·50B₂O₃ glass, respectively. A thin line represents transmittance of B₂O₃ glass. Numerical values show thickness of samples.

Fig. 2. Molar absorption coefficient of Bi₂O₃ and reflectance of Bi₂O₃-B₂O₃ and ZnO-Bi₂O₃-B₂O₃ glasses.

B₂O₃. The reflection peak energies observed in the reflection spectra, E_{ref} , are shown in Table 1.

4. Discussion

4.1 Relationship between absorption edge energy and reflection peak energy

The reflection spectrum of 50Bi₂O₃·50B₂O₃ glass showed a peak at about 4.0 eV, as depicted in Fig. 1. No absorption bands and reflection peaks were observed below 3.8 eV in the transmission and reflection spectra of 50Bi₂O₃·50B₂O₃ glass. These findings indicate that the absorption around absorption edge (3.01 eV) was the tail part of the absorption band observed in the reflection spectrum. The transmission spectrum of B₂O₃ glass showed no absorption bands at energies lower than 5.4 eV, although the interference pattern, probably due to the formation of very thin corrosion layers, and the gradual decrease in transmittance toward higher energies, probably due to the scattering of light by the corrosion layers, were observed. In addition, it has been reported that no remarkable

Fig. 3. Molar absorption coefficient of Bi₂O₃, absorption coefficient α and $(\alpha E)^{1/2}$ of 50Bi₂O₃·50B₂O₃ glass.

absorption is observed in the region below 5.4 eV in alkali borate glasses.²¹⁾ The absence of absorption bands below 5.4 eV indicates that the reflection peak at about 4.0 eV in 50Bi₂O₃·50B₂O₃ glass was due to Bi atoms. Since it is known that an absorption band due to Bi³⁺ ions is present in the region from 4.5 to 5.5 eV in Bi₂O₃-doped glasses,²²⁾ it was inferred that the reflection peak in the region from 3.7 to 4.6 eV originated from the absorption due to Bi³⁺ ions in the present glasses. That is, the absorption edge was due to the absorption by Bi³⁺ ions in the present glasses.

Figure 3 displays $(\alpha E)^{1/2}$ and α of 50Bi₂O₃·50B₂O₃ glass. α increased exponentially with an increase in energy in the energy region from 2.9 to 3.6 eV (α from 2×10^0 to 5×10^3 cm⁻¹, κ from 0.16 to 390 mol⁻¹ dm³ cm⁻¹). The exponential dependence of edge profile is characteristic of disordered materials.²⁰⁾ On the other hand, $(\alpha E)^{1/2}$ did not increase linearly with an increase in energy in the energy region lower than 3.6 eV, showing that the absorption edge profile did not obey the so-called Tauc's relation:²⁰⁾ $(\alpha E)^{1/2} \propto (E - E_{\text{edge}})$, in this region.

Since the absorption edge was due to the absorption by Bi³⁺ ions in the present glasses, it is natural that the absorption coefficient around absorption edge should be proportional to molar concentration of Bi³⁺ ions, c . In fact, the value of B was independent of c . Therefore, the absorption edge energy was obtained from the molar absorption coefficient of Bi₂O₃, κ .

Figure 4 shows the relationship between the absorption edge energy and the position of reflection peak. The absorption edge energy increased with an increase in energy of reflection peak with a proportional constant near unity (1.15). Therefore, it was inferred that the shift of absorption edge toward lower energy was due to the shift of the absorption band which caused the reflection peak in the region from 3.7 to 4.6 eV.

4.2 Relationship between absorption edge energy and electronegativity

Ingram and Duffy have defined the optical basicity expressed by Eq. (1) as a measure of average electron donation power of oxide ions in glass,²²⁾

Fig. 4. Relationship between absorption edge energy and reflection peak energy.

$$\Lambda_{\text{opt}} = \frac{6.94 - E_p}{3.57} = \frac{E_p - 6.94}{-3.57} \quad (1),$$

where Λ_{opt} and E_p represent the optical basicity of glass and the absorption peak energy of the Bi^{3+} ions obtained experimentally, respectively. This equation implies that the absorption peak energy shifts linearly toward lower energy with an increase in basicity of Bi-doped glasses, that is, with an increase in electron donation power of oxide ions and the decrease in ionicity of Bi–O bonds. In addition, they have shown that Λ_{opt} is related with the basicity assigned to individual oxides by Eq. (2),²²⁾

$$\Lambda_{\text{opt}} = \Lambda_{\text{th}} = \sum_i \Lambda_i X_i \quad (2),$$

$$\sum_i X_i = 1$$

where Λ_{th} , Λ_i and X_i are the theoretical basicity of glass, the basicity assigned to individual oxides i and the fraction of the amount of oxygen atoms in each constituent oxide i to the total amount of oxygen atoms in glass, respectively. Combining Eqs. (1) and (2) and letting $E_{\text{edge}} = E_p - \Delta$ gives Eq. (3),

$$E_{\text{edge}} = \sum_i (6.94 - \Delta - 3.57 \Lambda_i) X_i \quad (3),$$

where Δ represents the difference between E_{edge} and E_p . Δ is constant, since the absorption edge energy increases with an increase in reflection peak energy with a proportional constant of almost unity. It was anticipated from Eq. (3) that E_{edge} was expressed by the additivity rule with respect to X_i . **Figure 5** shows the relationship between E_{edge} obtained experimentally and that calculated from additivity rule using factors obtained by linear least-squares regression. It was found that E_{edge} obeyed the additivity rule with respect to X_i , with root mean square error of 0.02 eV and a maximum error of 0.05 eV. The additivity factors for E_{edge} , bracket term in Eq. (3), are listed in **Table 2**. It should be noted that E_{edge} obeyed the additivity rule with respect to, not only X_i but also the molar fraction of each oxide. Nevertheless, the additivity rule with respect to X_i was adopted in this discussion, since the additivity factor is related to electronegativity, as mentioned below.

Fig. 5. Comparison of absorption edge energy obtained experimentally and that calculated from additivity factors.

Table 2. Electronegativity, basicity, electronic polarizability of free ions and additivity factors for absorption edge energy

	χ_i	S_k		P_i / 10^{-3} nm^3		Λ_i from χ_i [Eq. (4)]	Additivity factors for absorption edge energy/eV
B	2.04	2.275	B ³⁺	0.0030	B ₂ O ₃	0.42	3.71 ± 0.01
Bi	2.02	2.342	Bi ³⁺	1.507	Bi ₂ O ₃	0.42	2.42 ± 0.02
Ga	1.81	2.419	Ga ³⁺	0.20	Ga ₂ O ₃	0.48	3.38 ± 0.12
Nb	1.6	1.42	Nb ⁵⁺	0.26	Nb ₂ O ₅	0.55	2.51 ± 0.13
Li	0.98	0.886	Li ⁺	0.029	Li ₂ O	1.03	1.27 ± 0.10
Na	0.93	0.835	Na ⁺	0.181	Na ₂ O	1.10	−0.04 ± 0.67
K	0.82	0.445	K ⁺	0.841	K ₂ O	1.32	−1.29 ± 1.32
Ca	1.00	0.946	Ca ²⁺	0.472	CaO	1.00	1.24 ± 0.67
Ba	0.89	0.683	Ba ²⁺	1.56	BaO	1.17	0.24 ± 0.67
Zn	1.65	2.223	Zn ²⁺	0.29	ZnO	0.54	2.79 ± 0.10
O		3.654					

χ_i : Pauling's electronegativity,²³⁾ S_k : Sanderson's electronegativity,³⁰⁾ Λ_i : basicity of each oxide, p_i : electronic polarizability of free ions.^{33),34)}

Duffy et al. have also proposed that Λ_i can be calculated from electronegativity by Eq. (4),²²⁾

$$\Lambda_i = \frac{3}{4(\chi_i - 0.25)} \quad (4),$$

where χ_i is the electronegativity of cationic atom in each oxide i in Pauling's scale. **Figure 6** shows the relationship between the additivity factor and Λ_i calculated from electronegativity²³⁾ by Eq. (4). The additivity factor decreased linearly with Λ_i with a slope of -4.68 , an intercept of 5.52 and a correlation coefficient of -0.97 , except Bi_2O_3 . The ratio of the slope to the coefficient of Λ_i in Eq. (4) was 1.3 ($-4.68/-3.57$) and was near unity, showing that E_{edge} depended on Λ_i . That is, E_{edge} was affected by the electron donation power of oxide ions which was governed by the electronegativity of cationic atoms, as expected in the concept of optical basicity. The factor for $X_{\text{Bi}_2\text{O}_3}$ was, however, much lower than that expected from electronegativity. This discordance indicates that the factor for $X_{\text{Bi}_2\text{O}_3}$ obtained experimentally includes the effect other than the electron donation power of oxide ions, which depends on $X_{\text{Bi}_2\text{O}_3}$. Therefore, it is expected that E_{edge} is expressed by the combination of Λ_{th} calculated from

Fig. 6. Relationship between additivity factor and A_i calculated from Pauling's electronegativity. A straight line was obtained by linear least regression without Bi data.

Fig. 7. Comparison of absorption edge energy obtained experimentally and that calculated from electronegativity derived basicity and $X_{\text{Bi}_2\text{O}_3}$.

Eq. (2) and another term which is proportional to $X_{\text{Bi}_2\text{O}_3}$. It was found from linear least-squares regression that E_{edge} was expressed by Eq. (5).

$$E_{\text{edge}} = 5.16 - 3.57 \sum_i A_i X_i - 1.24 X_{\text{Bi}_2\text{O}_3} \quad (5),$$

Figure 7 plots the E_{edge} calculated from Eq. (5) against that obtained experimentally. The root mean square error and the maximum error was 0.03 and 0.09 eV, respectively. The coefficient of $\sum A_i X_i$ in Eq. (5) agreed with that of A_i in Eq. (3). The coincidence of the coefficients supports the validity of Eq. (5).

Since $\sum A_i X_i$ and $X_{\text{Bi}_2\text{O}_3}$ varied from 0.42 to 0.50 and from 0.12 to 0.65, respectively, the changes in energy due to the changes in $\sum A_i X_i$ and $X_{\text{Bi}_2\text{O}_3}$ were 0.28 and 0.66 eV, respectively, in the present glasses. Therefore, it is inferred that the change in $X_{\text{Bi}_2\text{O}_3}$ has more effect on E_{edge} than basicity in the present glasses.

In a previous study, it was reported that Bi atoms were located around a Bi atom at a distance about 0.37 nm through the formation of Bi–O–Bi linkages and that their number was proportional to the atomic ratio of Bi atoms to oxygen atoms, that is, the two-thirds of $X_{\text{Bi}_2\text{O}_3}$, in Bi₂O₃–B₂O₃ and Li₂O–Bi₂O₃–B₂O₃ glasses.²⁴⁾ On the other hand,

Fig. 8. Comparison of absorption edge energy obtained experimentally and that calculated from δ_{O} and $X_{\text{Bi}_2\text{O}_3}$.

it has been shown that the nearest neighboring Bi atoms are located at 0.366 nm around a Bi atom in BaBi₃ crystal,²⁵⁾ indicating that the interaction between Bi atoms takes place at this distance. In addition, it has been shown from theoretical calculation that the interaction occurs at a distance of 0.390 nm between inter-molecular Bi atoms in BiMe₃ molecular crystal²⁶⁾ and at a distance of 0.368 nm between Bi–Bi atoms in α -Bi₂O₃ crystal.²⁷⁾ The similarity in Bi–Bi distance between these crystals and the present glasses is indicative of the presence of interaction between Bi atoms in the present glasses. Therefore, it was deduced that the bonding and antibonding interaction between Bi atoms took place, leading to a decrease in E_{edge} in the present glasses with increasing Bi₂O₃ content.²⁸⁾

Another measure of electron donation power of oxide ions is the partial charge of oxygen ions based on the electronegativity equalization principle proposed by Sanderson.^{29),30)} According to Sanderson, the partial charge of an oxide ion, δ_{O} , is calculated from the difference between the Sanderson's electronegativity of oxygen atom, S_{O} , and the average electronegativity, S_{av} , [Eq. (6)].

$$S_{\text{av}} = \Pi_k S_k^{x_k}$$

$$\delta_{\text{O}} = \frac{S_{\text{O}} - S_{\text{av}}}{1.57(S_{\text{O}})^{\frac{1}{2}}} \quad (6),$$

where x_k and S_k represents the atomic fraction of each constituent atom k and its electronegativity proposed by Sanderson, respectively. Although no correlation was observed between δ_{O} and E_{edge} (correlation coefficient; 0.24), E_{edge} was expressed by the combination of δ_{O} and $X_{\text{Bi}_2\text{O}_3}$, as shown in Fig. 8. In more detail, E_{edge} was expressed by Eq. (7), according to linear least-squares regression,

$$E_{\text{edge}} = 3.97 - 1.57\delta_{\text{O}} - 1.26X_{\text{Bi}_2\text{O}_3} \quad (7).$$

The root mean square error and the maximum error was 0.04 and 0.13 eV, respectively. The factor of $X_{\text{Bi}_2\text{O}_3}$ in Eq. (7) was very similar to that in Eq. (5), although δ_{O} and $\sum A_i X_i$ was somewhat scattered as shown in Fig. 9. This coincidence is due to the significant contribution of $X_{\text{Bi}_2\text{O}_3}$ on E_{edge} .

Fig. 9. Relationship between $\Sigma_i A_i X_i$ derived from Pauling's electronegativity and δ_O derived from Sanderson's electronegativity.

4.3 Relationship between absorption edge energy and refractive index

Duffy has proposed the basicity is related with the electronic polarizability of oxide ions which is derived from the molar refraction and the electronic polarizability of free cations, assuming that the polarizability of cations in solids is similar to that of free cations.^{31),32)} The basicity in glass is obtained from the refractive index by Eqs. (8a)–(8c),

$$R_m = \frac{(n^2 - 1)M}{(n^2 + 2)d} \quad (8a),$$

$$p(O^{2-}) = (3.97 \times 10^{-4} R_m - \sum_j s_j p_j) / t \quad (8b),$$

$$\Lambda_n = \frac{[3133p(O^{2-}) - 2.868]^{1/2}}{1.567} - 0.362 \quad (8c),$$

where, R_m , n , M , d , $p(O^{2-})$, p_j , s_j , t and Λ_n represent the molar refraction, the refractive index, the molecular weight, the density, the polarizability of oxide ion, the polarizability of cation j , the number of each cation j in the formula unit, the total number of oxide ions in the formula unit and the basicity obtained from refractive index, respectively. The polarizability of cations was obtained from Refs. 33),34). **Figure 10** shows the relationship between E_{edge} and Λ_n . Since although the data points for Li_2O – Bi_2O_3 – B_2O_3 glasses were somewhat scattered, the linear relationship was observed between E_{edge} and Λ_n , it was possible to predict E_{edge} from Λ_n with a root mean square error of 0.08 eV and a maximum error of 0.18 eV. This linear relationship was, however, caused by the linear relationship between Λ_n and $X_{\text{Bi}_2\text{O}_3}$ (**Fig. 11**) and the significant contribution of $X_{\text{Bi}_2\text{O}_3}$ to E_{edge} . Therefore, the combination of Λ_n and $X_{\text{Bi}_2\text{O}_3}$ reduced neither the root mean square error nor the maximum error. In order to reduce the errors, it is necessary to introduce the parameters other than $X_{\text{Bi}_2\text{O}_3}$, in case that Λ_n is adopted as ionicity to express the absorption edge energy in the present glasses.

The relationship between ionicity and refractive index has been studied in crystalline compounds by some researchers. Since Duffy has shown that $(n^2 + 2)^2$ is

Fig. 10. Relationship between absorption edge energy obtained experimentally and Λ_n obtained from refractive index. A straight line was obtained by linear least regression.

Fig. 11. Relationship between Λ_n and $X_{\text{Bi}_2\text{O}_3}$.

inversely proportional to band gap energy, E_g ,³⁵⁾ it is clear that Λ_n is related to E_g . On the other hand, Phillips and Van Vechten³⁶⁾ and Levine³⁷⁾ have shown that the susceptibility is inversely proportional to E_g^2 which is the sum of ionic and covalent contributions. Moreover, Wemple and DiDomenico have shown that $n^2 - 1$ of crystals is proportional to the dispersion energy, E_d , and inversely proportional to the average single oscillator gap energy, E_0 .³⁸⁾ E_d is proportional to the product of bond character, coordination number of cations and the number of valence electrons, and the E_0 is proportional to E_g . In this way, the relationship between refractive index and ionicity is very complicated. Therefore, further discussion on the relationship between E_{edge} and refractive index from the view point of ionicity is beyond the scope of the present study.

5. Conclusions

Absorption edge energy has been measured in the borate glasses containing a large amount of Bi_2O_3 . It was found that the absorption edge energy obeyed the additivity rule with respect to glass composition. The values of additivity factor depended on electronegativity of each constituent atom, except bismuth. It was deduced that the absorption

edge energy depended on the formation of Bi–O–Bi bonds between bismuth oxygen polyhedra, as well as on the ionicity of Bi–O bonds which was expressed by Duffy's optical basicity concept.

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