Composition dependence of absorption edge energy of borate glasses containing a large amount of Bi$_2$O$_3$

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Absorption edge energy has been studied in Bi$_2$O$_3$–B$_2$O$_3$, and (Li$_2$O, Na$_2$O, K$_2$O, CaO, BaO, ZnO, Ga$_2$O$_3$ and Nb$_2$O$_5$)–Bi$_2$O$_3$–B$_2$O$_3$ glasses containing a large amount of Bi$_2$O$_3$. 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$_2$O$_3$ was much smaller than that expected from electronegativity. The small value of additivity factor of Bi$_2$O$_3$ was discussed on the basis of Bi–O–Bi bond formation.

Key-words : Bismuth borate, Glass, Absorption edge energy

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.\(^1\)–\(^7\) 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.\(^8\) 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.\(^1\)–\(^7\) 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.\(^1\)–\(^3\) In bismuth-rich borate glasses, many researches have been conducted on the absorption edge energy.\(^1\)–\(^8\) It has been reported that the absorption edge energy shifted toward lower energy with increasing Bi$_2$O$_3$ content in Bi$_2$O$_3$–B$_2$O$_3$, Li$_2$O–Bi$_2$O$_3$–B$_2$O$_3$ and ZnO–Bi$_2$O$_3$–B$_2$O$_3$.\(^1\)–\(^3\) 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$_2$O$_3$ (Wako Chemicals, 99.9%), B$_2$O$_3$ (Kanto Chemicals, 95.0%), CaCO$_3$ (Kojundo Chemicals, 99%), BaCO$_3$ (Kojundo Chemicals, 99.5%), ZnO (High Purity Chemicals, 99.9%), Li$_2$O, CaO (Kojundo Chemicals, 99%), Na$_2$CO$_3$ (Kojundo Chemicals, 99%), K$_2$CO$_3$ (Kojundo Chemicals, 99%), Ga$_2$O$_3$ (Kisida, 99.999%) and Nb$_2$O$_5$ (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$_2$O$_5$–Bi$_2$O$_3$–B$_2$O$_3$ 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 50Bi$_2$O$_3$·50B$_2$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
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-
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 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 ions. 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 (αE)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 (or from 2 x 10⁰ to 5 x 10⁵ cm⁻¹, α 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, (αE)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) (αE)¹/² ∝ (E – E_{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 glasses.22)
where \( A_{\text{opt}} \) 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 \( A_{\text{opt}} \) is related with the basicity assigned to individual oxides by Eq. (2),

\[
A_{\text{opt}} = A_{\text{th}} = \sum_i A_i X_i
\]

where \( A_{\text{th}} \), \( A_i \) 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),

\[
E_{\text{edge}} = \sum_i \left( 6.94 - 3.57 A_i \right) X_i
\]

where \( \Delta \) represents the difference between \( E_{\text{edge}} \) and \( E_p \). \( \Delta \) 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 \( E_{\text{edge}} \) was expressed by the additivity rule with respect to \( X_i \). Figure 5 shows the relationship between \( E_{\text{edge}} \) obtained experimentally and that calculated from additivity rule using factors obtained by linear least-squares regression. It was found that \( E_{\text{edge}} \) 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 \( E_{\text{edges}} \) bracket term in Eq. (3), are listed in Table 2. It should be noted that \( E_{\text{edge}} \) obeyed the additivity rule with respect to \( X_i \) 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.

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

\[
A_i = \frac{3}{4(\chi_i - 0.25)}
\]
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 $E_{\text{edge}}$ was expressed by Eq. (5).

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

Figure 7 plots the $E_{\text{edge}}$ 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 $\Sigma A_i X_i$ in Eq. (5) agreed with that of $A_i$ in Eq. (3). The coincidence of the coefficients supports the validity of Eq. (5).

Since $\Sigma A_i X_i$ 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 $\Sigma A_i X_i$ 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 $E_{\text{edge}}$ 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 $\text{Bi}_2\text{O}_3$–$\text{B}_2\text{O}_3$ and $\text{Li}_2\text{O}$–$\text{Bi}_2\text{O}_3$–$\text{B}_2\text{O}_3$ glasses. It has been shown that the nearest neighboring Bi atoms are located at 0.366 nm around a Bi atom in $\text{BaBi}_3$ crystal, 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 $\text{BiMe}_3$ molecular crystal and at a distance of 0.368 nm between Bi–Bi atoms in $\alpha$-$\text{Bi}_2\text{O}_3$ crystal. 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 $E_{\text{edge}}$ in the present glasses with increasing $\text{Bi}_2\text{O}_3$ content.

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. According to Sanderson, the partial charge of an oxide ion, $\delta_O$, is calculated from the difference between the Sanderson’s electronegativity of oxygen atom, $S_O$, and the average electronegativity, $S_{av}$ [Eq. (6)].

$$S_{av} = \prod_k S_k^{x_k}; \quad \delta_O = \frac{S_O - S_{av}}{1.57(S_O)^2} \quad (6),$$

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 $\delta_O$ and $E_{\text{edge}}$ (correlation coefficient; 0.24), $E_{\text{edge}}$ was expressed by the combination of $\delta_O$ and $X_{\text{Bi}_2\text{O}_3}$, as shown in Fig. 8. In more detail, $E_{\text{edge}}$ was expressed by Eq. (7), according to linear least-squares regression.

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

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 $\delta_O$ and $\Sigma A_i X_i$ 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 $E_{\text{edge}}$. 

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**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 $X_{\text{Bi}_2\text{O}_3}$.

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

**Fig. 9.** Schematically shown the bond structure in $\text{Bi}_2\text{O}_3$ crystal. 

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4.3 Relationship between absorption edge energy and refractive index

Dufty 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),

\[ R_m = \frac{(n^2 - 1)M}{(n^2 + 2)d} \]  

(8a),

\[ p(O^{2-}) = (3.97 \times 10^{-4}R_m - \sum j(p_j)/t \]  

(8b),

\[ \Lambda_n = \frac{13133p(O^{2-}) - 2.8681^2}{1.567} = 0.362 \]  

(8c),

where, \( R_m, n, M, d, p(O^{2-}), p_j, s_j, t \) and \( \Lambda_n \) 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 \( \Lambda_n \). 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 \( \Lambda_n \) it was possible to predict \( E_{edge} \) from \( \Lambda_n \) 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 \( \delta_0 \) and \( X_{Bi_2O_3} \) (Fig. 11) and the significant contribution of \( X_{Bi_2O_3} \) to \( E_{edge} \). Therefore, the combination of \( \Lambda_n \) and \( X_{Bi_2O_3} \) 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 \( X_{Bi_2O_3} \), in case that \( \Lambda_n \) 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 Dufty has shown that \( (n^2 + 2)^2 \) is inversely proportional to band gap energy, \( E_g \), it is clear that \( \Lambda_n \) 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, \( E_0 \). 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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