Relationship between absorption edge and local structure around bismuth ions in bismuth-containing ternary phosphate and borate glasses

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1. Introduction

Lead-free low-Tg glasses with a high refractive index are of great interest in the fields of environmental load-reducing materials and optical glasses for low-energy precision molding. We have recently developed phosphate and borate glasses containing bismuth oxides as an agent for high-refractive-index and low-Tg optical glasses.1-4) Bismuth-containing glass, however, frequently has a yellowish color due to the 6s-6p transition of bismuth ions in the UV region. The optical basicity of glass has been proposed by Duffy and Ingram5) for understanding the optical absorption in the UV region for glasses with a very small amount of bismuth ions. However, it is not clear whether the concept is valid for glass containing a large amount of bismuth ions as one of the glass components. Recently, optical properties such as refractive index and absorption edge energy have been discussed in terms of optical basicity.6-7) We have reported the relationship between absorption edge energy (or reflection peak) and basicity in bismuth phosphate and bismuth borate glasses.6,9) In addition, we found that the basicity, that is, the degree of electron donation from glass, strongly correlated with the local structure around bismuth ions. This correlation was revealed by the 240 cm\(^{-1}\) Raman band due to a Bi\(^{3+}\)-related structure having a linear relationship with the absorption edge energy in ternary bismuth phosphate glass.7) However, it is still unclear how the structure around bismuth ions relates to absorption in other glass systems containing a large amount of bismuth oxide. In this study, we used Raman spectroscopy to investigate the local structure around bismuth ions and the optical absorption behavior in ternary bismuth phosphate and borate glasses.

2. Experimental procedure

Ternary phosphate \(aM_2O\cdot20Bi_2O_3\cdot(80-a)P_2O_5\) (\(M = Li, Na, K, Mg, Ca, Sr, Ba, Y, La, Nb, Zn, B, Al, Ga, In, Ge or Si\)) and borate \(bM_2O\cdot30Bi_2O_3\cdot(70-b)B_2O_3\) (\(M = Li, Na, K, Mg, Ca, Sr, Ba, Y, La, Nb, Zn, Al, Ga, In, Ge, Si or P\)) glasses were prepared by the conventional liquid-quench method. The nominal compositions of the glasses are listed in Tables 1(a) and 1(b). \(Bi_2O_3\) (Taiyo, 99.9%), \(B_2O_3\) (Kanto, 95%) and \(H_3PO_4\) (Wako, 85%) were used for the base materials. Metaphosphate sources (Rasa Ind.), \(R_2PO_3\) (\(R = Li, Na, K\)) (Wako, 99%), \(MCO_3\) (\(M = Ca, Sr, or Ba\)) (Kanto, 99%), \(La_2O_3\) (Kishida, 99.99%), \(Y_2O_3\) (Mitsuwa, 99.9%), \(Nb_2O_3\) (Wako, 99.9%), \(ZnO\) (Kojundo, 99.9%), \(Al_2O_3\) (Linde, 99.9%), \(Ga_2O_3\) (Kishida, 99.99%), \(In_2O_3\) (Kojundo, 99.99%), \(SiO_2\) (Sumitomo, 99.999%), \(GeO_2\) (Kishida, 99.999%), \(BPO_4\) (Yoneyama, 90.6%) were used as additive compositions for the phosphate glass. \(RNO_3\) (\(R = Li, Na, K\)) (Wako, 99%), \(MCO_3\) (\(M = Ca, Sr, or Ba\)) (Kanto, 99.9%), \(La_2O_3\) (Kishida, 99.99%), \(Y_2O_3\) (Mitsuwa, 99.9%), \(Nb_2O_3\) (Wako, 99.9%), \(ZnO\) (Kojundo, 99.9%), \(Al_2O_3\) (Linde, 99.9%), \(Ga_2O_3\) (Kishida, 99.999%), \(In_2O_3\) (Kojundo, 99.99%), \(SiO_2\) (Sumitomo, 99.999%), \(GeO_2\) (Kishida, 99.999%), \(BPO_4\) (Yoneyama, 90.6%) were used as additive compositions for both the borate and phosphate glasses. The mixture of starting materials was melted in a platinum crucible in ambient air for 2 h at 900–1250°C for phosphate glasses and 800–1100°C for borate glasses. Melting temperature was optimized to minimize the coloration due to reduction of bismuth ions. The optical transmittance of glass specimens with thickness of 3 mm was measured on a conventional spectrophotometer (Hitachi, U-4000). Absorption edge energy was determined by intersectional point of two lines extrapolated from the higher and lower energy sides in a molar extinction coefficient spectrum.7) Measurement...
of non-polarized Raman scattering spectra was performed by using a triple monochromator (Jobin-Yvon Horiba, T64000) equipped with solid-state laser (Coherent, Verde: 532 nm, 200 mW) in a backscattering arrangement. The spectra were corrected for the temperature- and frequency-dependent scattering intensity.\(^\text{10}\)

### 3. Results

The absorption edge energies of all the glass samples are listed in Tables 1(a) and 1(b), along with the theoretical optical basicity proposed by Duffy and Ingram.\(^\text{5}\) The relationships between the edge energy and basicity are shown in Figs. 1(a) and 1(b) for the
phosphate and borate glasses, respectively. The energy tended
to decrease with increasing basicity in the borate glasses. The
energy shifted toward the same direction in the phosphate glasses
as in the borate glasses. However, a steep linear relationship was
observed in the phosphate glasses with glass network-modifying
oxides and a gentle linear relationship was observed in those
with other oxides, as described in our previous report.7)

Figures 2(a) and 2(b), respectively, show the corrected Raman
spectra of 10Na2O·20Bi2O3·70P2O5 and 10Li2O·30Bi2O3·60B2O3
glasses as representative examples. Peaks due to phosphate
groups were observed above 600 cm⁻¹ in the phosphate glasses
as shown in Fig. 2(a). In the borate glasses, peaks due to borate
groups above 700 cm⁻¹ were observed as seen in Fig. 2(b).
Bismuth-related peaks were observed below 600 cm⁻¹ for phos-
phate glasses and below 700 cm⁻¹ for borate glasses. A peak was
clearly observed at 240 cm⁻¹ for the phosphate glasses, although
this peak was faint for borate glasses. A peak was
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4. Discussion

4.1 Absorption edge energy

The absorption edge energy shifted toward lower energies with
increasing glass basicity in both the borate and phosphate glasses
[Figs. 1(a) and 1(b)]. Therefore, Duffy’s concept of electron
donation seems to be basically valid even in the glasses con-
taining bismuth oxide as a major component of glass. In phos-
phate glasses, however, some modification of the effectiveness
of electron donation might be necessary to explain the two kinds
of relationships shown in Fig. 1(a), depending on the role of
additive oxides in the glass structure. The rates for the phosphate
system were 6.4 eV/basicity for glass network-modifying
oxides and 82 eV/basicity for glass network-forming oxides
as third additives.7) On the other hand, a single relationship
was observed in the borate system. The slope of the relationship
was 6.8 eV/basicity. Therefore, the value for the borate system
was similar to that for phosphate system with glass network-
modifying oxides. The value proposed by Duffy \[\Delta_{\text{Bi}} = \frac{(56000 - \nu)}{28800}: where \Delta_{\text{Bi}} and \nu
represent basicity and absorption peak position of Bi ions\]5) was
-3.6 eV/basicity; here, the relationships for the borate system and phosphate
system with the modifying oxides were of the same order as
in Duffy’s result. Therefore, the nature of electron donation to
the bismuth ions from oxide ions in bismuth-rich borate glasses
Gaussian peaks (named B1–B10) in the borate glasses, after sub-
stituting a 90 cm⁻¹ band of logarithmical shape which is assumed to
be a Boson peak. The peak positions are listed in the right
columns of Tables 1(a) and 1(b) for phosphate and borate glasses,
respectively. Peak positions for both the phosphate and borate
glasses differed by chemical composition.
and bismuth-rich phosphate glass with network-modifying oxides would be similar to the situation in the glasses including very small amount of bismuth ions studied by Duffy. However, we found that the addition of network-forming oxides to the bismuth phosphate system drastically changed the electron donation.

4.2 Raman peaks and their relationship with absorption edge energy

4.2.1 Bismuth phosphate system

Peaks P8–P14 above 600 cm⁻¹ for phosphate glass shown in Fig. 2(a) were assigned to vibration modes of phosphate, according to Raman spectroscopic studies on bismuth phosphate glasses by Jirak,11) Chahine11),12) and others.13),14) Peaks P7 and P8 at around 690 and 730 cm⁻¹ were assigned to symmetric stretching vibration in bridging oxygen between PO₂(Q2) units and to symmetric stretching vibration between PO₃(Q1) units, respectively. Peak P9 at 910–990 cm⁻¹ is attributed to asymmetric stretching vibration in Q₀ units and in chain end group of Q₁. Peak P10 at 1030–1070 cm⁻¹ was assigned to the vibration mode in chain end group of Q₁. Peaks P11–P12 and peaks P13–P14 at around 1160 and 1220 cm⁻¹, respectively, were assigned to symmetric vibration modes of Q₂ units and to non-bridging oxygen between Q₂ units.

On the other hand, peaks below 600 cm⁻¹, that is, peaks P1–P6 at around 150, 240, 320, 380, 500 and 590 cm⁻¹, were assigned to vibration modes related to bismuth ions according to Raman spectroscopic studies on bismuth-containing glasses and crystals.11)–18) Peaks P3 and P4 were attributed to the vibrations of Bi–O and Bi–O–Bi in distorted BiO₃ units, respectively. Peaks P5 and P6 were due to Bi–O⁺ stretching vibration in distorted linked BiO₃ unit. Peak P2 was due to the symmetric stretching anion motion in the angularly constrained cation-anion-cation configuration in the BiO₃ unit. A weak shoulder (peak P1) located at 160 cm⁻¹ was attributed to heavy metal Bi³⁺ ion vibration in BiO₃ and BiO₆ or to the translational mode (lattice vibration).

Peak wavenumbers of all peaks are plotted against theoretical basicity of glass in Fig. 3(a). Only the 1060 cm⁻¹ peak among all the peaks assigned to phosphate groups was shifted toward higher wavenumber with increasing glass basicity. The shift indicates an increase of bond strength in the chain end group of Q₁.

The bismuth-related peaks P2–P6 at 240, 320, 380, 500 and 590 cm⁻¹ shifted toward higher wavenumber with increasing basicity, while the peak at 160 cm⁻¹ shifted toward lower wavenumber.

Hardcastle19) has proposed that the Bi–O vibration energy increases with decreasing Bi–O bond length, on the basis of the correlation between Bi–O stretching frequency and Bi–O bond length in bismuth mixed oxide crystals. Therefore, the shift of peaks P2–P6 toward higher wavenumber indicates the decrease of bond length. This implies an increase in bond strength30) and an increase in covalent character of the Bi–O bond. The shifts of peaks P2–P6 was about 10 cm⁻¹ in the present basicity range, corresponding to a change in Bi–O length of the order of 0.01 Å. Moreover, the difference in the extent of the peak shift between peaks P2–P4 and P5–P6 indicates that the electron donation in the bridging Bi–O–Bi structure seems to be similar to that in the Bi–O⁻ terminated structure.

On the other hand, the reason for the shift toward lower energy of peak P1 with basicity is not yet clear. Since, peak intensity increased with the bismuth oxide content in the glass, a certain structure including bismuth atoms is surely the origin of this peak. Here, no structural models are proposed regarding the origin of this peak. However, it is expected from the structure of bismuth phosphate crystals31),32) that an increase of bismuth oxides causes the coupling of bismuth oxygen polyhedra in glass. Therefore, one likely explanation that the low vibration energy is due to the vibration of a cluster composed of bismuth oxygen.

![Fig. 3. Position of deconvoluted Raman peaks plotted against theoretical basicity of glass for (a) ternary phosphate glasses and (b) ternary borate glasses.](image-url)
polyhedra, which is weakly connected around glass structure. The origin of this peak is further discussed in the next section, since this peak was observed much more clearly in the borate glasses.

4.2.2 Bismuth borate glasses

Peaks B6–B10 above 700 cm\(^{-1}\) for borate glasses [Fig. 2(b)] were assigned to vibration modes of boron structure according to Raman spectroscopic studies on bismuth borate glasses by Bale\(^{20,21}\), Bai\(^{22,23}\) and other researchers\(^{24-29}\). Peak B7 located from 770 to 860 cm\(^{-1}\) was assigned to a breathing vibration of a ring structure containing both BO\(_3\) and BO\(_2\) units. Peak B8 at 930 cm\(^{-1}\) was attributed to the vibration of orthoborate groups. Peak B9 at 1020–1080 cm\(^{-1}\) was assigned to the normal vibration of tri-, tetra- and penta-borate groups. Peak B10 at 1310–1330 cm\(^{-1}\) was assigned to symmetric vibration modes in B-O-B and terminal B-O in pyroborate groups, and to B-O stretching vibration in various borate groups.

Peaks below 700 cm\(^{-1}\), that is, peaks B1–B5 around 150, 270, 390, 570 and 640 cm\(^{-1}\), were assigned to vibration modes related to bismuth ions, similarly to phosphate glasses. The peaks related to bismuth ions in the borate glasses were located at higher wavenumber than those in phosphate glasses except peaks B1 and B1. It is reasonable that the Bi-O vibrations coupled with a borate network are located at higher wavenumber than those coupled with phosphate networks, since a B atom is lighter than a P atom\(^{30}\).

Peak B3 at around 390 cm\(^{-1}\) was attributed to the vibrations of Bi-O and Bi-O-B in distorted BiO\(_3\) units. This peak was located at almost the same wavenumber as peaks P3 and P4 in phosphate glasses. The shape of the peak around this wavenumber was broad, so the contour might be composed of multiple peaks. The contour, however, could not be resolved into multiple peaks. We treated the contour as one peak, B3. Peak B4 around 570 cm\(^{-1}\) is due to Bi-O' stretching vibration in a distorted linked BiO\(_3\) unit. This peak has the same origin as peak P5 in the phosphate glasses. Peak B5 at around 640 cm\(^{-1}\) was assigned Bi-O' stretching vibration in BiO\(_3\) units. This peak would be the same origin as peak P6 in phosphate glasses. Peak B2 at around 270 cm\(^{-1}\) was assigned to the symmetric stretching anion motion in angularly constrained cation-anion-cation configuration in BiO\(_3\) unit, which will be the same origin as peak P2 in phosphate glasses. Peak B1 at 150 cm\(^{-1}\) was intense in the borate glasses, and the vibration mode seemed localized, as reflected in the narrow peak width. In addition, the position of peak P1 was very similar to that of peak B1, indicating that the position of these peaks was less affected by the surrounding structure. These findings are consistent with the peak at 150 cm\(^{-1}\) being due to clusters consisting of bismuth oxygen polyhedra.

Peaks B2–B5 related to bismuth ions shifted toward higher wavenumber with increasing basicity, although peak B1 at 150 cm\(^{-1}\) shifted toward lower wavenumber. In the previous study\(^7\), it was shown that the dependence of the P2 peak position on the glass basicity was affected by the structural role of the third additives in the phosphate glasses. It is, however, inappropriate to discuss this effect in the borate glass, since peak B2 was too weak to obtain the precise peak position by deconvolution. Therefore, we compared the general trend of peak shifts with changing basicity. The direction and magnitude of the shift of peaks B2–B5 in borate glasses are highly consistent with the results for phosphate glasses. The shift might originate in an increase in Bi-O bond strength by electron donation from oxide to bismuth ions as in the phosphate glasses. The linear shift toward higher energy of the absorption edge with basicity [Figs. 1(a) and 1(b)] indicates a linear relationship between absorption edge energy and Raman peak positions (P2–P6 and B2–B5) in phosphate and borate glasses, respectively. Changes in Bi-O bond length according to the study by Hardcastle were of the order of 0.01 Å in both phosphate and borate glasses. This means that the effect of third additive oxides on electron donation was similar in both of the glass systems. This effect is supported by the fact that the edge shifts against basicity are almost the same value; that is, −6.4 eV/basicity in the phosphate system and −6.8 eV/basicity in the borate system. The vibration energy of peak B1 decreased with increasing basicity in borate glasses as the peak P1 in phosphate glasses. The negative shifts of peaks P1 and B1 might indeed be due to the weakening of the interaction between the clusters of bismuth oxygen polyhedra and the glass structure surrounding them. This peak seemed to lack a direct relationship with the shift toward higher energy of the absorption edge. Peak B1 was much more obvious than peak P1 in each spectrum, indicating that Bi tended to form Bi oxygen polyhedral clusters more easy in borate glass than in phosphate glass, as seen in a bismuth borate glass with lower bismuth content than the present glass\(^{23,26}\).

5. Conclusions

Raman spectroscopy was used to study the relationship between the absorption edge energy and glass structure around bismuth ions in ternary bismuth phosphate and borate glasses. The absorption energy shifted toward lower energy with increasing theoretical basicity in both phosphate and borate glasses. Raman peaks related to bismuth ions shifted toward higher wavenumber with increasing theoretical basicity of glass, suggesting a decrease in Bi-O bond length, that is, an increase in bond strength. The peak at around 150 cm\(^{-1}\) in the borate and phosphate glasses shifted toward lower wavenumber with basicity.

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