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## FULL PAPER

Colorless Bi<sub>2</sub>O<sub>3</sub>-containing borophosphate glasses with high refractivityKatsuki Hayashi<sup>1</sup>, Grégory Tricot<sup>2</sup> and Akira Saitoh<sup>1,†</sup><sup>1</sup>Graduate School of Science and Engineering, Ehime University, Matsuyama, Ehime 790–8577, Japan<sup>2</sup>Laboratoire de Spectroscopie pour les Interactions, la Réactivité & l'Environnement (LASIRE)–UMR CNRS 8516, Université de Lille, F-59000 Lille, France

The effects of P<sub>2</sub>O<sub>5</sub> substitution on the coordination structure of a Bi<sup>3+</sup> in Bi<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> glasses were examined by applying <sup>11</sup>B and <sup>31</sup>P MAS-NMR spectroscopy. Observation of the wide optical bandgap after the substitution revealed a substantial difference in the solvation shell structure between the P<sub>2</sub>O<sub>5</sub> substituted and the P<sub>2</sub>O<sub>5</sub>-free Bi<sub>2</sub>O<sub>3</sub>-containing glasses, i.e., the P<sub>2</sub>O<sub>5</sub> substitution replaced by the B<sub>2</sub>O<sub>3</sub> is effective for forming the solvation shell, which leads to weak ligand field around a Bi<sup>3+</sup>. We report the optical properties of the Bi<sub>2</sub>O<sub>3</sub>–P<sub>2</sub>O<sub>5</sub>–B<sub>2</sub>O<sub>3</sub> glass providing a wide optical bandgap (~3.6 eV) and high refractive index (~2.0).

Key-words : Borophosphate glass, Refractive index, Nuclear magnetic resonance, Structure

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## 1. Introduction

Bi<sub>2</sub>O<sub>3</sub>-containing oxide glasses are widely employed in applications for optical devices.<sup>1)</sup> Although Bi<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> glasses that have many excellent physical properties are a highly desired host for optically active ions,<sup>2)–4)</sup> their fatal drawback is coloration.<sup>5),6)</sup> This issue, ascribed to a strong ligand field around a cation, was resolved by a co-doping technique.<sup>7),8)</sup> For instance, Saitoh et al. demonstrated the “solvation shell” model based on directly observing the ligand structures of Ce<sup>3+</sup> and Er<sup>3+</sup> in SiO<sub>2</sub> glasses to understand the striking doping effects of P<sub>2</sub>O<sub>5</sub>. The concept of solvation shell of ions in the SiO<sub>2</sub> glass, i.e., preferential coordination of doped P<sub>2</sub>O<sub>5</sub> around the rare-earth ions, is favorable for designing highly efficient luminescence as an optical material. As a result, the photoluminescence properties of Ce<sup>3+</sup> and Er<sup>3+</sup> in those samples showed a slight Stokes shift and high emission intensity. Hence, we can consider the substitution of B<sub>2</sub>O<sub>3</sub> by P<sub>2</sub>O<sub>5</sub> in the Bi<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> glasses as effective in realizing colorless property, keeping a high refractive index, which will weaken the ligand field of a Bi<sup>3+</sup>.

Little qualitative structure by the effect of P<sub>2</sub>O<sub>5</sub> has been reported in the binary Bi<sub>2</sub>O<sub>3</sub>–P<sub>2</sub>O<sub>5</sub> glasses because of the narrow glass formation region up to 40 mol% of Bi<sub>2</sub>O<sub>3</sub>.<sup>5),9),10)</sup> It is considered that the borophosphate glasses consisting of tetrahedrally coordinated PO<sub>4</sub>–BO<sub>4</sub>–PO<sub>4</sub> linkage can widen the glass formation region<sup>4),11)</sup> and thus offer the possibility of providing high refractive index materials.

The purpose of this study is to present Bi<sub>2</sub>O<sub>3</sub>–P<sub>2</sub>O<sub>5</sub>–

B<sub>2</sub>O<sub>3</sub> glasses with high concentrations of Bi<sub>2</sub>O<sub>3</sub>, wide optical bandgap, and high refractive index. In addition, the glass network was characterized by <sup>11</sup>B and <sup>31</sup>P MAS-NMR spectroscopies to determine the substitution effect of P<sub>2</sub>O<sub>5</sub> on the coordination structure around a Bi<sup>3+</sup>.

## 2. Experimental

Glass samples were prepared using the conventional melt-quenching method. Reagent grades of Bi<sub>2</sub>O<sub>3</sub> (99.99%), B<sub>2</sub>O<sub>3</sub> (99.9%), and BiPO<sub>4</sub> (99.9%) were used as raw materials. The nominal molar composition is  $x\text{Bi}_2\text{O}_3\text{-}y\text{P}_2\text{O}_5\text{-(}100-x-y\text{)B}_2\text{O}_3$  with  $40 \leq x \leq 60$ ,  $0 \leq y \leq 20$ . Batches that yielded 12–15 g were mixed and then melted for 30 min at 1000 °C in an alumina crucible in an electric furnace in the air. The dissolution of Al<sub>2</sub>O<sub>3</sub> into the sample was 1–2 mol% by SEM-EDS. The melts were poured into a preheated stainless-steel mold and then annealed to remove residual thermal stress in the air for 24 h at 360–470 °C, depending on glass transition temperatures. The amorphous nature of the resulting bulk glasses was confirmed by X-ray diffraction analysis.

The density of the bulk sample was determined using the Archimedes method with kerosene as an immersion liquid for the glasses at room temperature. The estimated uncertainties due to composition fluctuations were ±0.01 g/cm<sup>3</sup>.

The refractive index was measured using the refractometer for a 3 × 3 × 10 mm<sup>3</sup> rectangular glass rod at 587.6 nm wavelengths. The estimated uncertainties due to composition fluctuations were ±0.01. Optical transmission spectra were measured using a 1 mm-thick plate and a ~2 μm thick film. The film was obtained from a piece of glass balloon blown from each glass melt using an alumina pipe.

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The <sup>11</sup>B and <sup>31</sup>P MAS-NMR experiments were performed at 256.7 and 323.9 MHz on an 18.8 T spectrometer (AVANCE III, Bruker) using a 3.2-mm probe head operating at a spinning frequency of 20 kHz. The <sup>11</sup>B MAS-NMR spectra were obtained with a  $\pi/10$  flip angle of 1.0  $\mu$ s, recycle delay (rd) of 5 s, and 1024 transients. The <sup>31</sup>P MAS-NMR spectra were obtained with a  $\pi/6$  flip angle of 1.8  $\mu$ s, rd of 120 s, and 32 transients. The <sup>11</sup>B and <sup>31</sup>P chemical shifts are respective to NaBH<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> as -42.06 and 0 ppm, respectively. The NMR spectra were decomposed using the dmfit software<sup>12)</sup> to extract the chemical shift and relative proportions parameters.

### 3. Results and discussion

Figures 1(a) and 1(b) show the compositional dependences of the density and refractive index measured at 587.6 nm of wavelength in the  $x\text{Bi}_2\text{O}_3\text{-}y\text{P}_2\text{O}_5\text{-(}100-x-y\text{)B}_2\text{O}_3$  glasses. In each Bi<sub>2</sub>O<sub>3</sub> concentration sample, the density and refractive index decrease with increasing P<sub>2</sub>O<sub>5</sub>, which replaces B<sub>2</sub>O<sub>3</sub>. Note that the  $x = 60, y = 10$  sample particularly presents a high refractive index ( $\sim 2.1$ ) measured at 587.6 nm and a small photoelastic constant ( $+0.5 \times 10^{-12} \text{ Pa}^{-1}$ ) measured at 632.8 nm.

Figures 2(a)–2(c) show the compositional dependences of optical transmission spectra of the  $x\text{Bi}_2\text{O}_3\text{-}y\text{P}_2\text{O}_5\text{-(}100-x-y\text{)B}_2\text{O}_3$  glasses. The optical absorption edges of the Bi<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub> glasses blueshift, substituting B<sub>2</sub>O<sub>3</sub> with P<sub>2</sub>O<sub>5</sub>. While the optical absorption edges of the Bi<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub> glasses redshift with increasing Bi<sub>2</sub>O<sub>3</sub> concentration. The samples of large concentrations of Bi<sub>2</sub>O<sub>3</sub> ( $x$ ) and small amount of P<sub>2</sub>O<sub>5</sub> ( $y$ ) are likely to show pale yellow. Figure 2(d) compares the transmission spectra of the bulk and thin film samples. Notably, the  $x = 50, y = 20$  sample presents the absorption edge being near a deep ultraviolet region ( $< 350 \text{ nm}$ ).<sup>13)</sup>

Figures 3(a) and 3(b) show the compositional dependences of the absorption coefficient spectra and Tauc plots determined from the absorption coefficients of the 50Bi<sub>2</sub>O<sub>3</sub>-50B<sub>2</sub>O<sub>3</sub> ( $x = 50, y = 0$ ) and the 50Bi<sub>2</sub>O<sub>3</sub>-20P<sub>2</sub>O<sub>5</sub>-30B<sub>2</sub>O<sub>3</sub> ( $x = 50, y = 20$ ) glasses. Note that the optical bandgaps

are determined from the Tauc plot  $(\alpha h\nu)^{1/2}$  versus photon energy  $h\nu$ , where  $\alpha$  denotes the optical absorption coefficient. Here, the photon energy dependence of the optical absorption of glass can be expressed as  $(h\nu - E)^2/h\nu$ , where  $E$  denotes the optical band gap.<sup>14)</sup> The optical band-gap of the 50Bi<sub>2</sub>O<sub>3</sub>-20P<sub>2</sub>O<sub>5</sub>-30B<sub>2</sub>O<sub>3</sub> glass increases by  $\sim 0.2 \text{ eV}$  with the incorporation of P<sub>2</sub>O<sub>5</sub>.

Figures 4(a)–4(c) show <sup>11</sup>B MAS-NMR spectra, including the proportions of three- and four-coordinated borate units of the  $x\text{Bi}_2\text{O}_3\text{-}y\text{P}_2\text{O}_5\text{-(}100-x-y\text{)B}_2\text{O}_3$

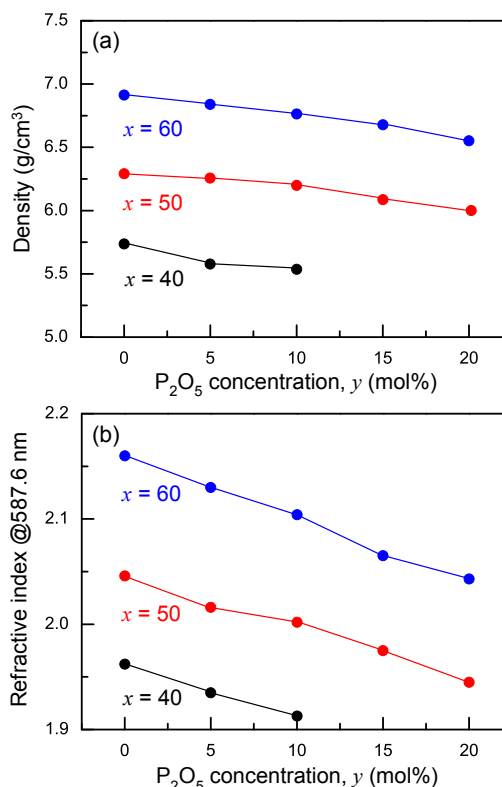


Fig. 1. Compositional dependences of the (a) density and (b) refractive index of the  $x\text{Bi}_2\text{O}_3\text{-}y\text{P}_2\text{O}_5\text{-(}100-x-y\text{)B}_2\text{O}_3$  ( $40 \leq x \leq 60, 0 \leq y \leq 20$ ) glasses.

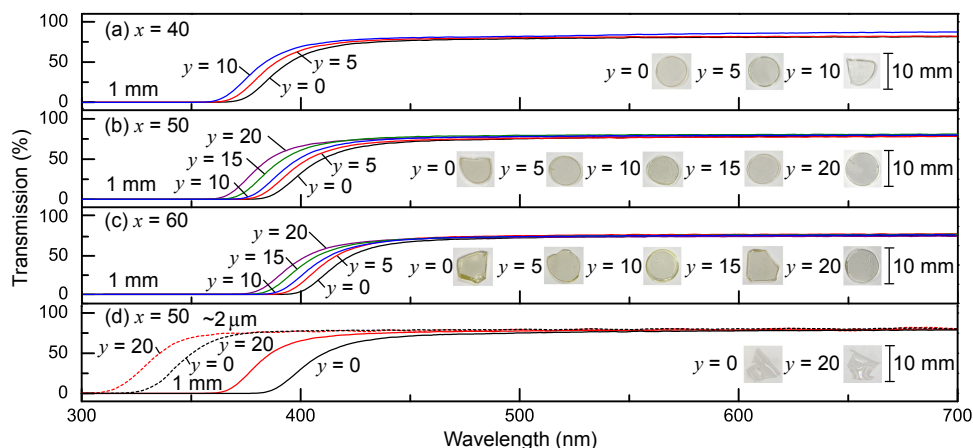
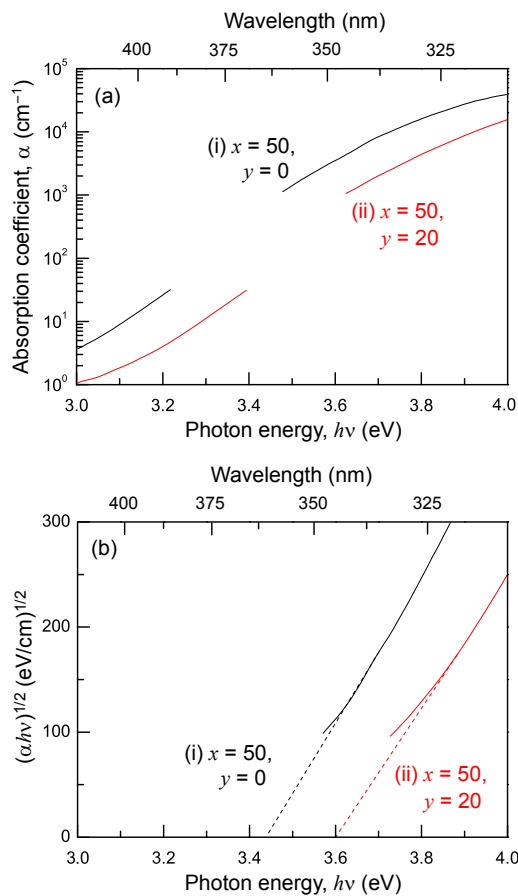


Fig. 2. Compositional dependences of optical transmission spectra of the  $x\text{Bi}_2\text{O}_3\text{-}y\text{P}_2\text{O}_5\text{-(}100-x-y\text{)B}_2\text{O}_3$  ( $40 \leq x \leq 60, 0 \leq y \leq 20$ ) glasses in the wavelength range 300–700 nm for samples with 1 mm and  $\sim 2 \mu\text{m}$  thicknesses. The dashed lines in (d) present the spectra for the film samples of  $x = 50, y = 0, 20$ .

glasses. Altogether, five different species can be observed with four  $B^{IV}$  and one  $B^{III}$  units. The assignments of each borate unit<sup>(4),15)</sup> are listed in **Table 1**, and are derived from a 1D/2D NMR protocol applied to a similar system ( $SnO-B_2O_3-P_2O_5$ ) in a previous study.<sup>4)</sup> As the concentrations of  $Bi_2O_3$  ( $x$ ) and substituted  $P_2O_5$  ( $y$ ) increase, the apparent ratio of  $B^{III}$  appears to increase. However, there is no clear regularity in the ratio of  $B^{III}$  to  $B^{IV}$ , and the ratio tends to increase within the error of the deconvolution of  $^{11}B$  NMR spectrum. On the other hand, the proportions of each unit of  $B^{IV}_{(1)}-B^{IV}_{(4)}$  do not essentially depend on the changes in  $Bi_2O_3$  and  $P_2O_5$  concentrations. However, the  $x = 50$  and



**Fig. 3.** (a) Absorption coefficient spectra and (b) Tauc plots of the  $50Bi_2O_3-50B_2O_3$  and  $50Bi_2O_3-20P_2O_5-30B_2O_3$  glasses with 1 mm and  $\sim 2\ \mu m$  thickness. In (b), the dashed lines present the estimated optical bandgap of the  $x = 50, y = 0$  and  $x = 50, y = 20$  samples.

$y = 20$  sample shows a large proportion of  $B^{IV}$ ; among them, the proportion of  $B^{IV}_{(2)}$  and  $B^{IV}_{(3)}$  is substantial. The experiments show that our glasses mainly contain three coordinated boron species ( $>65\%$ ). The low proportion of  $B^{IV}_{(1)}$  ( $<5\%$ ) indicates a strong  $B^{IV}/B^{III}$  mixing. Moreover, the four-coordinated B is also adjacent to a  $Bi^{3+}$  as revealed by the significant presence of  $B^{IV}_{(3)}$  unit.

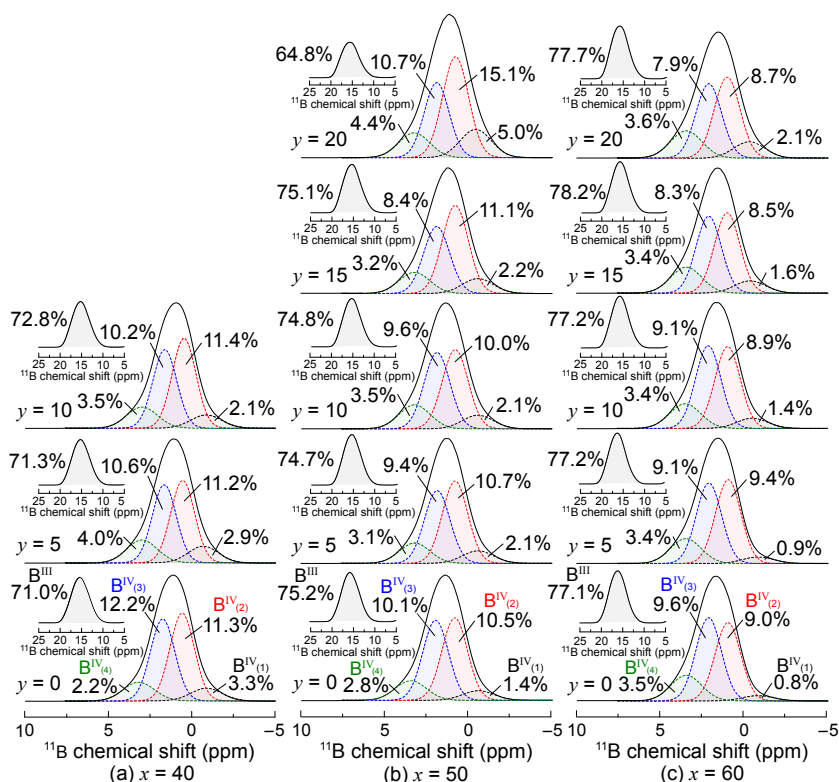
**Figures 5(a)–5(c)** show the  $^{31}P$  MAS-NMR spectra with the proportions of phosphate units in the  $xBi_2O_3-yP_2O_5-(100-x-y)B_2O_3$  glasses. Three species around  $-18, -10,$  and  $3$  ppm can be observed with various proportions depending on the glass composition. The assignments of these three species are reported in Table 1 and are derived from the 1D/2D NMR protocol applied to the tin borophosphate glass containing a high amount of  $SnO$ .<sup>4)</sup> As the concentration of  $Bi_2O_3$  ( $x$ ) increases, the proportion of  $Q^1$  decreases. On the other hand, as the concentration of  $P_2O_5$  ( $y$ ) increases,  $Q^0$  and  $Q^0_B$  decrease, and  $Q^1$  increases. The  $x = 50$  and  $y = 20$  sample shows that  $Q^0_B$  and  $Q^1$  units are major species of the phosphate units.

According to the  $^{31}P$  NMR spectra, the four-coordinated P is bound to the three- and four-coordinated B from the assignment of  $Q^0_B$ . The four coordinated P is terminated to a  $Bi^{3+}$  as a  $Q^1$  or  $Q^0$  unit. Hence, the coordination of the  $Bi^{3+}$  in the  $50Bi_2O_3-20P_2O_5-30B_2O_3$  glass consists of  $PO_4$  or  $BO_4$  units. When the amount of  $P_2O_5$  substitution is large,  $PO_4$  is the primary ligand, which can be similar to the solvation shell structure by  $P_2O_5$ .<sup>7),8)</sup>

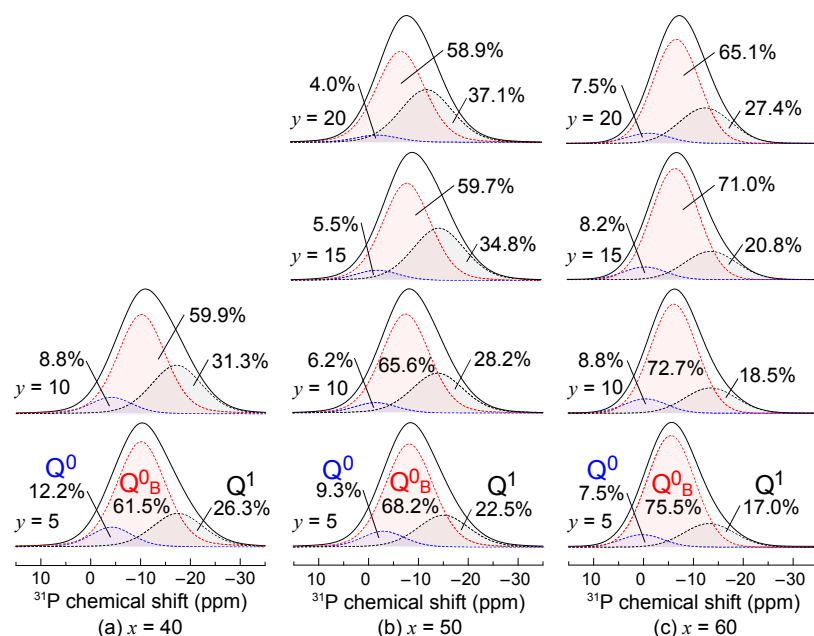
**Figure 6** illustrates the coordination structure model of the borate and phosphate units in the vicinity of a  $Bi^{3+}$  in the  $50Bi_2O_3-20P_2O_5-30B_2O_3$  ( $x = 50, y = 20$ ) glass, which has an optical bandgap of 3.6 eV and a refractive index of 2.0. A possibility of the formal charges on the non-bridging oxygens (NBOs) belonging to the phosphate units is  $-1/2$  of the  $Q^1$  and  $Q^0$  units. Because in a middle phosphate group, an electron is delocalized over two NBOs via  $p\pi-d\pi$  bonding. In other words, in the phosphate units, the formal charge on the NBO in the P–O bond is  $-0.5$  due to the delocalization of electrons over the two NBOs via the  $Op\pi-P3d\pi$  bond.<sup>7),16),17)</sup> Then, ligands around a  $Bi^{3+}$  belong to this type of oxygens with the formal negative charge of  $-0.5$ , which is an intermediate value between conventional NBO ( $-1$ ) and bridging oxygen ( $0$ ). Therefore, the ligand field is considered weaker because the  $Bi^{3+}$  surroundings are not composed of large formal charged oxygens ( $-1$ ). On the other hand, in the

**Table 1.** Assignments of each borate and phosphate unit were analyzed by the  $^{11}B$  and  $^{31}P$  MAS-NMR spectra of the  $xBi_2O_3-yP_2O_5-(100-x-y)B_2O_3$  glasses

Units and notation		Assignments	Refs.
Borate	$B^{IV}_{(1)}$	Connected to tetrahedral species $[B(OX^{IV})_4]$ with $X = P$ or $B$	4, 15
	$B^{IV}_{(2)}$	Connected to at least one $B^{III}$ units $[B(OX^{IV})_m(OB^{III})_k]$ ( $0 \leq m \leq 3, 1 \leq k \leq 4$ )	
	$B^{IV}_{(3)}$	Direct coordination to at least one $Bi^{3+}$	
	$B^{IV}_{(4)}$	Not assigned	
Phosphate	$Q^1$	Pyrophosphate unit with three non-bridging oxygen ions per phosphorus and one connected P atom	4
	$Q^0_B$	$PO_4$ tetrahedral unit with one bridging oxygen with to $B^{III}$ or $B^{IV}_{(1)}$ and no connected P atom	
	$Q^0$	Orthophosphate unit with four non-bridging oxygen ions per phosphorus	



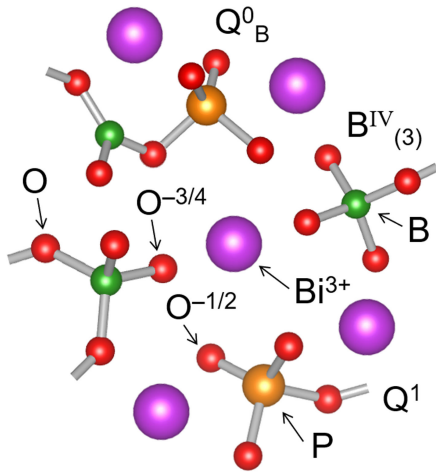
**Fig. 4.** <sup>11</sup>B MAS-NMR spectra of the  $x\text{Bi}_2\text{O}_3\text{-}y\text{P}_2\text{O}_5\text{-(}100-x-y\text{)B}_2\text{O}_3$  glasses with (a)  $x = 40$ ,  $y = 0, 5$ , and  $10$ , (b)  $x = 50$ ,  $y = 0, 5, 10, 15$ , and  $20$ , and (c)  $x = 60$ ,  $y = 0, 5, 10, 15$ , and  $20$ . The B<sup>III</sup> and B<sup>IV</sup> (B<sup>IV</sup><sub>(1)</sub>–B<sup>IV</sup><sub>(4)</sub>) proportions are denoted, respectively. The notations (B<sup>III</sup> and B<sup>IV</sup><sub>(1)</sub>–B<sup>IV</sup><sub>(4)</sub>) indicate the coordination number of oxygens in superscript and type in parenthesis.



**Fig. 5.** <sup>31</sup>P MAS-NMR spectra of the  $x\text{Bi}_2\text{O}_3\text{-}y\text{P}_2\text{O}_5\text{-(}100-x-y\text{)B}_2\text{O}_3$  glasses with (a)  $x = 40$ ,  $y = 5$  and  $10$ , (b)  $x = 50$ ,  $y = 5, 10, 15$ , and  $20$ , and (c)  $x = 60$ ,  $y = 5, 10, 15$ , and  $20$ . The Q<sup>0</sup>, Q<sup>0</sup><sub>B</sub>, and Q<sup>1</sup> proportions are denoted, respectively. The notations (Q<sup>0</sup>, Q<sup>0</sup><sub>B</sub>, and Q<sup>1</sup>) indicate the number of non-bridging oxygens in superscript.

BO<sub>3</sub> and BO<sub>4</sub> units, the charge of  $-1$  is allocated to each oxygen if it is a three-coordinated oxygen, and the charge of  $-3/4$  if it is a four-coordinated oxygen to compensate for the  $+3$  charge of B. If BO<sub>4</sub> units were involved in the

coordination in part, they would contribute to forming a weak ligand field since the net charge would be  $-3/4$ .<sup>18)</sup> The fact that the coordination structure around a Bi<sup>3+</sup> in the 40Bi<sub>2</sub>O<sub>3</sub>–60P<sub>2</sub>O<sub>5</sub> glass resembles a BiPO<sub>4</sub> crystal<sup>5),19)</sup>



**Fig. 6.** The coordination structure model of a  $\text{Bi}^{3+}$  in the colorless and high refractive  $50\text{Bi}_2\text{O}_3-20\text{P}_2\text{O}_5-30\text{B}_2\text{O}_3$  ( $x = 50$ ,  $y = 20$ ) glass, deduced from the analyses of  $^{11}\text{B}$  and  $^{31}\text{P}$  MAS-NMR spectroscopy.

is supportive evidence of a strong affinity for phosphate units.

Finally, it is worth noting the relationship between optical properties and coordination structure. Lone pair electrons of  $\text{Bi}^{3+}$  occupy the top of the valence band in crystalline  $\text{Bi}_2\text{O}_3$ ,<sup>19)</sup> which may compete with the O 2p electron level. Hence, the optical absorption derived from the  $\text{Bi}^{3+}$   $6s^2-6s^1p^1$  transition<sup>5),19)</sup> strongly correlates to the coordination structure around a  $\text{Bi}^{3+}$ . Therefore, the bandgap energy increase by decreasing the negative charge on the ligand oxygen. This idea agrees with the observed widened optical bandgap by substitution of  $\text{P}_2\text{O}_5$ .

#### 4. Conclusions

The colorless, high refractive index  $\text{Bi}_2\text{O}_3-\text{P}_2\text{O}_5-\text{B}_2\text{O}_3$  glass is realized by substitution  $\text{B}_2\text{O}_3$  by  $\text{P}_2\text{O}_5$ . The results are summarized as follows:

- (1) The  $50\text{Bi}_2\text{O}_3-20\text{P}_2\text{O}_5-30\text{B}_2\text{O}_3$  glass has a larger optical bandgap ( $\sim 3.6$  eV) and high refractive index ( $\sim 2.0$ ).
- (2) The contrast in optical transmission spectra of the  $50\text{Bi}_2\text{O}_3-20\text{P}_2\text{O}_5-30\text{B}_2\text{O}_3$  glass to that of the  $50\text{Bi}_2\text{O}_3-50\text{B}_2\text{O}_3$  glass is understood because the  $\text{Bi}^{3+}$  in former glass has a solvation shell structure regulated by the phosphate anions.
- (3) A weak ligand field is attributed to the less net charge belonging to NBOs of  $\text{O}^{-1/2}$  or  $\text{O}^{-3/4}$  around a  $\text{Bi}^{3+}$ .
- (4) The  $\text{Bi}_2\text{O}_3-\text{P}_2\text{O}_5-\text{B}_2\text{O}_3$  glasses with a wide optical bandgap, high refractive index, and small photoelastic constant are preferred to optical lenses and filters in the visible region.

#### 5. Declaration of competing interests

The authors declare to have no interest in the present paper.

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