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Mössbauer and ESR Studies of Potassium Borophosphate Glasses

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A linear decrease in isomer shifts of Fe^{3+} and Fe^{2+} was observed with an increase in alkali content of borophosphate glasses. The decrease is attributed to a change in the role of iron from a network modifier to a network former, or a decrease in the interatomic distance between iron and oxygen atoms. A linear decrease in quadrupole splitting and linewidth was also observed with increasing alkali content, and the decrease is attributed to the increased symmetry around iron nucleus. A linear decrease in relative absorption area of Fe^{2+} in Mössbauer spectra was also observed with increasing alkali content of the glasses. This result is attributed to an increased oxidation atmosphere brought about by alkali oxide into BPO_4 units. Gamma-ray irradiation (1×10^8 R) experiments resulted in no change in these Mössbauer parameters, indicating that the glasses are less sensitive to γ-rays than borate or phosphate glasses. ESR absorption intensity of PO_4^{2-} observed in γ-ray irradiated, iron-free borophosphate glasses increased linearly with an increase in the alkali content in the lower alkali region, and the increase is attributed to a linear increase in the fraction of non-bridging oxygen in PO_4 tetrahedra constituting BPO_4 (and PO_4) units.

Mössbauer studies of borate glasses[1-6] suggested formation of non-bridging oxygen (NBO) to start at an alkali content of 20 mol%. The fraction of NBO constituting BO_4 or FeO_4 tetrahedra was obtained from the Mössbauer absorption area of Fe^{2+} produced by γ-ray irradiation of borate glasses[5] containing a small amount of iron, and also from the absorption area of a hyperfine structure in partially relaxed spectra observed at low temperature.[6] These two results are well consistent with each other, within the experimental error, and the fraction of NBO proved to increase linearly with increasing alkali content of the borate glasses in the alkali region$\geqslant$20 mol%. Gamma-ray irradiation experiments of borate glasses containing 7 mol% of Fe_2O_3 resulted in an increase in *s*-electron density at the iron nucleus,[3] and this was confirmed from the reduction of Fe^{3+} to Fe^{2+} in γ-ray irradiated borate glasses[3,5] containing a small amount of Fe_2O_3. Mössbauer and ESR studies of potassium phosphate glasses[7,8] were also performed to investigate the formation of NBO in these glasses, and a continuous increase in relative absorption area of Fe^{2+} in the Mössbauer spectra was attributed to an increase in the fraction of NBO. This was also confirmed from a linear increase in ESR absorption intensity of PO_4^{2-} radicals in γ-ray irradiated, iron-free phosphate glasses.[7] The γ-ray irradiation experiments also resulted in a decrease in the Mössbauer absorption area of Fe^{2+} ions.[8] As for borophosphate glasses, it is well known that the glasses are essentially composed of BPO_4 units[9] in which individual boron and phosphorus atoms are tetrahedrally bonded with oxygen atoms to form BO_4 and PO_4 tetrahedra.

The present study was carried out to investigate the formation of NBO and γ-ray irradiation effects in borophosphate glasses.

Experimental

All the glass samples denoted by a formula $xK_2O\cdot(100-x)(B_2O_3,P_2O_5)\cdot7Fe_2O_3$ were prepared by fusing the individual mixture of weighed quantitities of K_2CO_3, H_3BO_3, $NH_4H_2PO_4$, and Fe_2O_3 of guaranteed reagent grade at 1200 °C for 3 h in an electric muffle furnace. Prior to this fusion, the mixture in a platinum crucible was calcined at 800 °C for 30 min. The value of *x* was changed from 10 to 50, and the molar ratio of P_2O_5 to B_2O_3 was so chosen as to be 1.0 and 2.0. Transparent and dark brown glasses were prepared by quenching the platinum crucible with cold water in a beaker. All the glass sample prepared in this way were confirmed to be amorphous by X-ray diffractometry, and they were preserved in a desiccator filled with dry nitrogen gas to protect them from the atmospheric moisture.

These glasses were exposed to γ-rays of 1×10^6 R and 1×10^8 R with a dose rate of 1×10^6 R/h at the ambient temperature in the ^{60}Co-γ ray irradiation facilities of Kyushu University and Japan Atomic Energy Research Institute. During the irradiation each glass sample was kept in a polyethylene bag filled with dry nitrogen gas, and the bag was placed in a glass tube filled with nitrogen gas and silica gel.

Mössbauer measurements were performed by the constant acceleration method at room temperature, with a source of cobalt-57 diffused into a palladium foil. A pure iron foil enriched with iron-57 was used to calibrate the velocity of spectrometer and for the reference of isomer shift. All the Mössbauer spectra were fitted to Lorenzian lineshapes by computer calculations. ESR measurements (X-band) of γ-ray irradiated borophosphate glasses were performed at room temperature in the National Universities' Laboratory for the Common Use of the JAERI Facilities, and also in Kyushu University. The magnetic field was calibrated by using JEOL standard material of MgO : Mn^{2+}.

Results and Discussion

Each of the Mössbauer spectra for potassium borophosphate glasses consists of two quadrupole doublets due to Fe^{3+} and Fe^{2+} ions. Isomer shifts for both the iron species are shown in Fig. 1 as a function of the alkali content of the borophosphate glasses having a P_2O_5/B_2O_3 ratio of 1.0. It is seen from Fig. 1 that both the Fe^{3+} and Fe^{2+} ions are primarily surrounded by six oxygen atoms just like in phosphate glasses.[7,8,10-12] Iron will therefore be present at the interstitial site of the three dimensional network structure of BPO_4 units constituted by BO_4 and PO_4 tetrahedra, facing to two or three NBOs. A linear decrease in isomer shift (Fig. 1) is attributed to an increase in covalency of both iron species, probably because the coordination number of some parts of iron changes from 6 to 4 with the

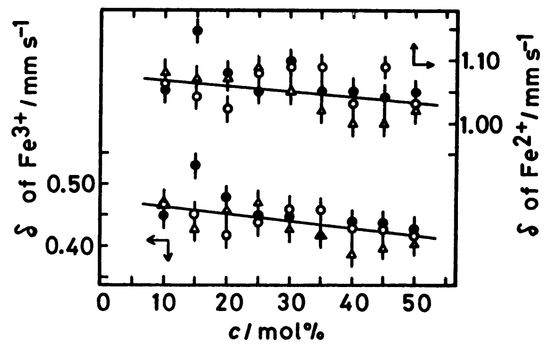

Fig. 1. Isomer shift of Fe^{2+} (above) and Fe^{3+} (below) plotted against the alkali content (c) of potassium borophosphate ($P_2O_5/B_2O_3=1.0$) glasses.
○: Non-irrad., ●: 1×10^6 R irrad., △: 1×10^8 R irrad.

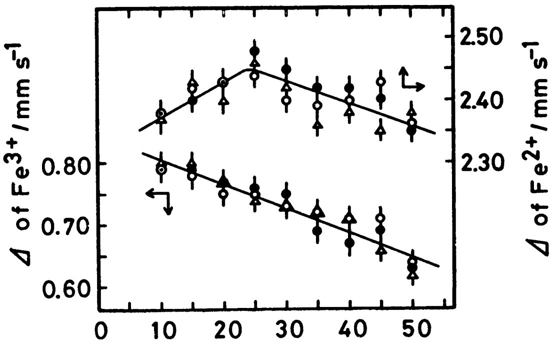

Fig. 2. Quadrupole splitting of Fe^{2+} (above) and Fe^{3+} (below) plotted against the alkali content of potassium borophosphate ($P_2O_5/B_2O_3=1.0$) glasses.
○: Non-irrad., ●: 1×10^6 R irrad., △: 1×10^8 R irrad.

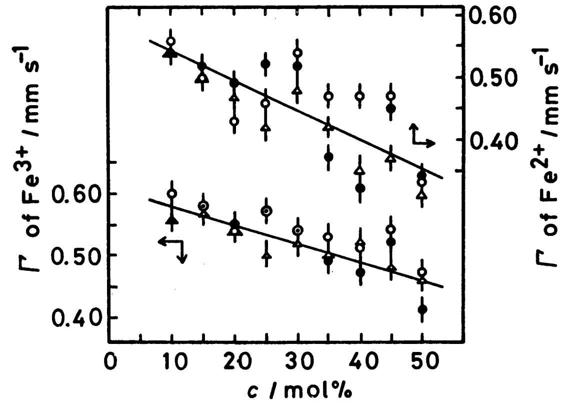

Fig. 3. Linewidths of Fe^{2+} (above) and Fe^{3+} (below) plotted against the alkali content of potassium borophosphate ($P_2O_5/B_2O_3=1.0$) glasses.
○: Non-irrad., ●: 1×10^6 R irrad., △: 1×10^8 R irrad.

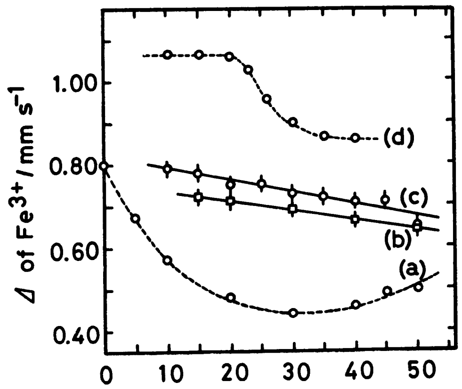

Fig. 4. Quadrupole splitting of Fe^{3+} in glasses.
(a): Potassium phosphate, (b): potassium borophosphate ($P_2O_5/B_2O_3=2.0$), (c): potassium borophosphate ($P_2O_5/B_2O_3=1.0$), (d): potassium borate.

increase in the alkali content of the glasses.[10–12] This change in the coordination number means the formation of FeO_4 tetrahedra in which iron plays a role of network former, instead of a network modifier at the interstitial site. Another possible reason for the increase in the covalency is a decrease in the interatomic distance between iron and oxygen, produced by the introduction of alkali oxide into BPO_4 units.

Quadrupole splitting values for both the iron species are plotted against the alkali content of the borophosphate glasses ($P_2O_5/B_2O_3=1.0$) in Fig. 2, where the values decrease linearly with increasing alkali content. The decrease in quadrupole splitting of Fe^{3+} (high spin) means the increase in the symmetry around the iron nucleus because each d-orbital of Fe^{3+} ion is occupied by one electron and therefore the effect of valence electrons on the electric field gradient can be negligible. Quadrupole splitting for Fe^{2+} ion also decreased in the alkali region $\geqslant$25 mol%, and the decrease is attributed to the increase in the symmetry around the iron nucleus. An increase in the quadrupole splitting of Fe^{2+} ion in the lower alkali region is difficult to explain, but the alkali content at which quadrupole splitting shows a distinct maximum, *i.e.*, 25 mol%, is well consistent with that in the composition dependence of ESR intensity of PO_4^{2-} to be discussed later.

Linewidth (FWHM) values for Fe^{3+} and Fe^{2+} ions also show a linear decrease when the alkali content of the glasses increases (Fig. 3). The broad linewidth for iron in glasses is attributed to the non-uniformity of the steric configuration around the individual iron nucleus.[12–14] The decrease in linewidth therefore suggests that the steric configuration around iron nucleus becomes more uniform as the fraction of alkali oxide increases in these borophosphate glasses. It is seen from the Mössbauer results Figs. (1—3) for the γ-ray irradiated borophosphate glasses that iron atoms in these glasses are not affected by γ-ray irradiation up to 1×10^8 R. This is inconsistent with the results of borate[3] or phosphate[8] glasses where a decrease in isomer shift of Fe^{3+} or a linear decrease in the absorption area of Fe^{2+} ions was observed by γ-ray irradiation. These results lead to a conclusion that the borophosphate glasses are less sensitive to γ-rays than the parent borate or phosphate glasses.

Mössbauer studies of potassium borophosphate glasses with a P_2O_5/B_2O_3 ratio of 2.0 were also performed. These results are summarized in Table 1. Isomer shifts and linewidths are well consistent with the corresponding values of the borophosphate glasses with a P_2O_5/B_2O_3

TABLE 1. MÖSSBAUER PARAMETERS FOR THE POTASSIUM BOROPHOSPHATE ($P_2O_5/B_2O_3=2.0$) GLASSES

$X^{a)}$ / mol%	Species	$\delta^{b)}$ / mm s^{-1}	$\Delta^{c)}$ / mm s^{-1}	$\Gamma^{d)}$ / mm s^{-1}	$A^{e)}$ / %
15	Fe^{3+}	0.45	0.72	0.56	74.2
15	Fe^{2+}	1.09	2.42	0.54	25.8
20	Fe^{3+}	0.45	0.71	0.53	74.1
20	Fe^{2+}	1.10	2.49	0.53	25.9
30	Fe^{3+}	0.45	0.69	0.55	76.4
30	Fe^{2+}	1.09	2.44	0.52	23.6
40	Fe^{3+}	0.44	0.66	0.48	78.7
40	Fe^{2+}	1.04	2.37	0.41	21.3
50	Fe^{3+}	0.42	0.65	0.48	86.7
50	Fe^{2+}	1.01	2.26	0.41	13.3

a) Alkali content of the glasses. b) Isomer shift. c) Quadrupole splitting. d) Linewidth. e) Absorption area.

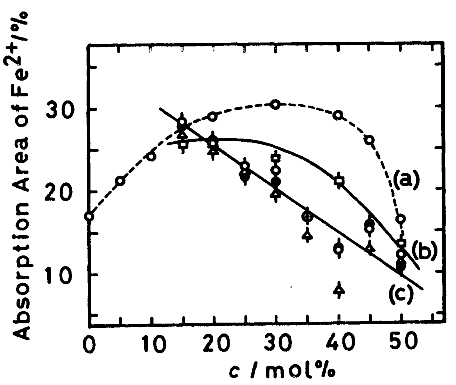

Fig. 5. Mössbauer absorption area of Fe^{2+} in glasses.
(a): Potassium phosphate, (b): potassium borophosphate ($P_2O_5/B_2O_3=2.0$), (c): potassium borophosphate ($P_2O_5/B_2O_3=1.0$).
○: Non-irrad., ●: 1 × 10^6 R irrad., △: 1 × 10^8 R irrad.

ratio of 1.0. Quadrupole splitting values of Fe^{3+} ions in these borophosphate glasses are also shown in Fig. 4, where the previous results on borate and phosphate glasses are shown for comparison. It is obvious from Fig. 4 that the quadrupole splitting values for the borophosphate glasses are intermediate between those for the borate and phosphate glasses, and that the values increase when the concentration of B_2O_3 increases. These results suggest that the symmetry around iron nucleus decreases with the introduction of B_2O_3 into phosphate glasses of which network comprises only PO_4 units, probably because the network structure becomes more complicated as a result of the formation of BPO_4 units in which equal numbers of BO_4 and PO_4 tetrahedra are arranged alternately. The network structure is considered to be more complicated for the borophosphate glasses with an P_2O_5/B_2O_3 ratio higher than 1.0 because the network is composed of both PO_4 and BPO_4 units.

TABLE 2. ESR PARAMETERS FOR THF PO_4^{2-} RADICAL IN THE POTASSIUM BOROPHOSPHATE ($P_2O_5/B_2O_3=1.0$) GLASSES

$X^{a)}$ / mol%	$g^{b)}$	$A^{c)}$ / G	$I^{d)}$
15	2.01	41	1.1
18	2.01	41	1.2
20	2.01	41	1.3
25	2.01	40	1.6
30	2.01	38	1.2
40	2.01	34	0.9
45	2.01	33	0.8

a) Alkali content of the glasses. b) g-value. c) Coupling constant. d) Peak intensity.

TABLE 3. ESR PARAMETERS FOR THF PO_4^{2-} RADICAL IN THF POTASSIUM BOROPHOSPHATE ($P_2O_5/B_2O_3=2.0$) GLASSES

$X^{a)}$ / mol%	$g^{b)}$	$A^{c)}$ / G	$I^{d)}$
18	2.01	41	1.7
20	2.01	41	1.9
30	2.01	39	2.7
40	2.01	35	2.2
50	2.01	32	1.7

a) Alkali content of the glasses. b) g-value. c) Coupling constant. d) Peak intensity.

Absorption areas of Fe^{2+} ions in these glasses are shown in Fig. 5, in which a linear decrease in the absorption area is observed with increasing alkali content for the borophosphate glasses having a P_2O_5/B_2O_3 ratio of 1.0. This is quite different from the results for phosphate glasses, in which formation of NBO was speculated.[7,8] The decrease in the absorption area is attributed to an increased oxidation atmosphere brought about by the introduction of alkali oxide into BPO_4 units in which all the boron and phosphorus atoms are singly bonded with oxygen atoms to form BO_4 and PO_4 tetrahedra.[9] It is seen from the results for the borophosphate glasses with a P_2O_5/B_2O_3 ratio of 2.0 (Fig. 5; curve 5b is intermediate between 5a and 5c) that some parts of iron are in the environment similar to that of phosphate glasses. This is explained by the presence of PO_4 units as well as BPO_4 units because one half of phosphorus atoms can be assumed to be present as PO_4 units having P=O double bonds when the P_2O_5/B_2O_3 ratio is 2.0.

The ESR spectrum of γ-ray (1 × 10^8 R) irradiated, iron-free borophosphate glasses consists of an almost isotropic doublet. The g value and hyperfine coupling constant of ^{31}P were found to be 2.01 and 41-32 G (1 G = 10^{-4} T), respectively. The doublet has been attributed to PO_4^{2-} radical[7,15-20] produced by X-ray or γ-ray irradiation. As is shown in our previous paper,[7] the absorption intensity of PO_4^{2-} can be correlated with the fraction of NBO in PO_4 units because the energy level for the electrons on NBO is known to be higher than that on bridging oxygen[21] and therefore more electrons will be scattered by γ-ray irradiation in the former. The ESR results are summarized in Tables 2 and 3, from which a decrease in coupling constant of PO_4^{2-} doublet is seen when the alkali content of borophosphate glasses exceeds 25 or 30 mol%. This is identical with the decrease in the absorption intensity of the PO_4^{2-}

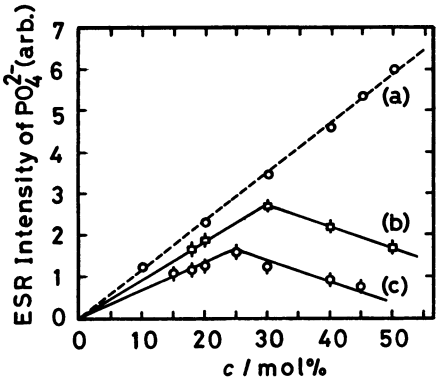

Fig. 6. ESR absorption intensity of PO_4^{2-} in glasses. (a): Potassium phosphate, (b): potassium borophosphate ($P_2O_5/B_2O_3=2.0$), (c): potassium borophosphate ($P_2O_5/B_2O_3=1.0$).

radical, *i.e.*, the intensity shows a distinct maximum at 25 or 30 mol% when the P_2O_5/B_2O_3 ratio is 1.0 or 2.0, respectively. This is shown in Fig. 6, where the result of phosphate glasses[7] which are free from iron is also shown for comparison. Figure 6 demonstrates that the concentration of PO_4^{2-} radical in borophosphate glasses increases with increasing alkali content in the lower ($x \leq 25$ or 30 mol%) alkali region. This is the same as the result of phosphate glasses (Fig. 6a). The increase in the absorption intensity of the PO_4^{2-} radical is therefore attributed to a linear increase in the fraction of NBO in PO_4 tetrahedra constituting BPO_4 units for the borophosphate glasses with a P_2O_5/B_2O_3 ratio of 1.0, of which composition is expressed as $x K_2O \cdot (100-x) BPO_4 \cdot 7Fe_2O_3$. It is very noteworthy that the absorption intensity shows a maximum at an alkali content of 25 mol%, which is not observed in the study of phosphate glasses. The decrease in the absorption intensity in the alkali region higher than 25 mol% will be attributed to the formation of NBO in BO_4 tetrahedra which are the other component of BPO_4 units, although the formation could not be confirmed in the present study. It is therefore considered that the formation reaction of NBO in borophosphate glasses is competitive between PO_4 and BO_4 tetrahedra, and that the formation in PO_4 tetrahedra is predominant in the alkali region lower than 25 mol%, *i.e.*, in such an alkali region that the K_2O/BPO_4 ratio is less than one third. This is also the case for the borophosphate glasses with a P_2O_5/B_2O_3 ratio of 2.0 of which composition is expressed as $x K_2O \cdot 2/3(100-x) BPO_4 \cdot 1/3(100-x) P_2O_5 \cdot 7Fe_2O_3$. That is to say, formation of NBO at PO_4 tetrahedra in BPO_4 units is predominant until 18 mol% ($K_2O/BPO_4=1/3$) and then the formation in PO_4 units of which environment is essentially the same as that of phosphate glasses will be predominant in the alkali region of 18—30 mol%. It is then considered in borophosphate glasses that the fraction of NBO bonded with phosphorus atoms is increased with increasing fraction of P_2O_5.

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