^{57}Fe Mössbauer and DTA study of $\text{R}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glasses (R = Li, Na)

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The ^{57}Fe Mössbauer spectra of $x\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ and $x\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glasses ($x = 0, 0.5, 1.0$ and 1.5) consist of two doublets due to Fe^{II} and Fe^{III} . The isomer shift indicates that Fe^{III} atoms form $\text{Fe}^{\text{III}}\text{O}_4$ tetrahedra or $\text{Fe}^{\text{III}}\text{O}_6$ octahedra, while Fe^{II} atoms from $\text{Fe}^{\text{II}}\text{O}_6$ octahedra. A linear relationship exists between the glass transition temperature, T_g , and the quadrupole splitting, Δ , of Fe^{III} atoms in the Mössbauer spectra. Slopes of the straight lines were estimated to be 460 and $370^\circ\text{C} (\text{mm s}^{-1})^{-1}$ in $x\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ and $x\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glasses, respectively. These results suggest that Fe^{III} atoms form oxygenpolyhedra that are intermediate between $\text{Fe}^{\text{III}}\text{O}_4$ tetrahedra and $\text{Fe}^{\text{III}}\text{O}_6$ octahedra. The electric conductivity obtained by a dc four-probe method was of the order of 10^{-5} to $10^{-6} \text{ S cm}^{-1}$.

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1. Introduction

Among lithium-ion insertion compounds, LiCoO_2 , LiNiO_2 and LiMn_2O_4 are now commercially used as a 4.0 V cathode material for lithium-ion battery. Recently, phospho-olivine type LiMPO_4 compounds (M = Fe, Mn, Co or Ni) have been investigated intensively.^{1)–4)} Among them an olivine-type LiFePO_4 has attracted much interest as a new cathode material for lithium-ion battery because of its high theoretical capacity (170 mAh/g), operating at potential of 3.4 V vs. Li^+/Li , and because iron is less toxic and less expensive than cobalt and nickel.^{1)–3)} NaFePO_4 is known to have a maricite-type structure.⁵⁾ The difference of the structure between maricite-type and olivine-type compounds is that Na^+ ions occupy 4c Wyckoff site and Fe^{II} atoms 4a sites in NaFePO_4 , whereas Li^+ and Fe^{II} respectively occupy 4c and 4a sites in LiFePO_4 . In addition, the average of Na–O bond length in the former is longer than the Li–O length in the latter, although Fe–O and P–O bond length are comparable to each other in these two compounds.⁵⁾

Vanadate glasses are known to have semiconductivity caused by electron hopping from V^{IV} to V^{V} .⁶⁾ Vanadium pentoxide (V_2O_5) is known to have a layered structure composed of VO_5 pyramids.⁶⁾ ^{57}Fe Mössbauer spectra of vanadate glasses proved that quadrupole splitting of Fe^{III} atoms, which share oxygen atoms with V^{IV} and V^{V} , reflect the change of the local symmetry or distortion of $\text{Fe}^{\text{III}}\text{O}_4$ and VO_4 tetrahedra.

A linear relationship between the glass transition temperature, T_g , and the quadrupole splitting, Δ , of Fe^{III} in the Mössbauer spectra is very effective for determining the site occupation of Fe^{III} atoms in oxide and non-oxide glasses.^{7)–10)} This linear relationship, termed T_g - Δ Rule by Nishida⁷⁾ gives a slope of $680^\circ\text{C} (\text{mm s}^{-1})^{-1}$ when Fe^{III} atoms occupy tetrahedral sites as network former (NWF), as observed in several oxide glasses like silicate, aluminate and vanadate glasses, while the slope becomes 260°C

$(\text{mm s}^{-1})^{-1}$ when Fe^{III} atoms occupy octahedral NWF sites as observed in tungstate glasses.^{7)–11)} On the other hand, much smaller slope of $35^\circ\text{C} (\text{mm s}^{-1})^{-1}$ is obtained when Fe^{III} occupying network modifier (NWM) sites, as in phosphate, sulfate and fluoride glasses.^{7),10),11)} The different slope of the straight line suggests that the chemical bond of NWF-oxygen polyhedra is much more intense than that of NWM-oxygen polyhedra and also the chemical bond of NWF-oxygen tetrahedra is more intense than that of NWF-oxygen octahedra since the former is more covalent than the latter. In this paper, Mössbauer spectra of $x\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ and $x\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glasses ($x = 0, 0.5, 1.0$ and 1.5), developed for a cathode material of Li-ion battery, were measured for determining the local structure Fe^{III} .

2. Experimental

$x\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ and $x\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glasses ($x = 0, 0.5, 1$, and 1.5) were prepared by melt-quenching method with a stoichiometric amount of Li_2CO_3 (or Na_2CO_3), FeO , V_2O_5 and P_2O_5 . Each reagent mixture was placed in a porcelain crucible with an additional amount (5%) of charcoal, and was melted at 1100°C for 45–60 min under a nitrogen atmosphere. Homogeneous glass samples were prepared by quenched between two cold copper plates. The ^{57}Fe Mössbauer spectra were measured at room temperature with a 370 MBq of ^{57}Co (Pd) source. A sheet of metallic iron foil ($\alpha\text{-Fe}$) was used as a reference for the isomer shift, δ , and for calibrating the velocity scale of the spectrometer. Glass transition temperature was determined by DTA conducted at a heating rate of $10^\circ\text{C min}^{-1}$ using $\alpha\text{-Al}_2\text{O}_3$ powder for the temperature calibration. The electric conductivity, σ , was measured by a dc four-probe method at room temperature with a sample which was cut into a rectangle copper wires were attached to the sample with silver paste and silver-containing lead solder.

3. Results and discussion

The ^{57}Fe Mössbauer spectra of $x\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glasses ($x = 0, 0.5, 1.0$ and 1.5) are shown in **Fig. 1**. Mössbauer param-

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Fig. 1. Mössbauer spectra of $x\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ ($x = 0, 0.5, 1.0$ and 1.5) glasses measured at room temperature.

eters obtained for these glasses are described in **Table 1**. Outer doublet observed in $2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glass (Fig. 1, top) has δ and Δ values of $1.14 (\pm 0.01)$ and $2.20 (\pm 0.02) \text{ mm s}^{-1}$, respectively, indicating the presence of Fe^{II} atoms form $\text{Fe}^{\text{II}}\text{O}_6$ octahedra.^{7–12} The δ and Δ values of $0.39 (\pm 0.01)$ and $1.21 (\pm 0.02) \text{ mm s}^{-1}$, respectively, obtained for the inner doublet in Fig. 1 (top) indicate $\text{Fe}^{\text{III}}\text{O}_4$ tetrahedra.^{7–13} The linewidth (FWHM), Γ , values for Fe^{II} and Fe^{III} in $2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glass (Fig. 1, top) were 0.73 and 0.52 mm s^{-1} , respectively (Table 1). Comparable Γ values of 0.51 – 0.54 mm s^{-1} were obtained for Fe^{III} in $2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$, $0.5\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ (Fig. 1, second), $\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$

(Fig. 1, third) and $1.5\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glasses (Fig. 1, bottom). Γ values for Fe^{II} in these glasses were in the range of 0.59 – 0.62 mm s^{-1} (Table 1). All these values prove that both Fe^{III} and Fe^{II} atoms constitute a glassy phase,^{6,10–12} since the criterion between glassy and crystalline phases are located at about 0.40 mm s^{-1} , for example, Γ values of several crystalline compounds and glass ceramics are indicated at 0.25 – 0.30 mm s^{-1} .^{6–13}

Absorption areas, A , for Fe^{II} and Fe^{III} in $2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glass were estimated to be 78.1% and 21.9% , respectively. Figure 1 shows that the absorption area for Fe^{II} decreases with an increasing Li_2O content, i.e., from 78.1 to 59.6 , 55.9 and 51.5% , as observed in $0.5\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$, $\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ and $1.5\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glasses, respectively. This result will be associated with a formation of nonbridging oxygen (NBO) in PO_4 and VO_4 units, i.e., a cleavage of the network causes an electron transfer from Fe^{II} to NBO, which is supported that Γ values for Fe^{II} atoms were decreasing gradually by increasing Li_2O contents, i.e., from 0.73 to 0.62 , 0.60 and 0.59 , as observed in $2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$, $0.5\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$, $\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ and $1.5\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glasses, respectively. As a result, the fragments of VO_4 and PO_4 units will migrate from a higher energy sites with Fe^{II} atoms to a lower energy sites with VO_4 and/or PO_4 units in the super-cooled liquid state, since the structural relaxation of $\text{Fe}^{\text{II}}\text{O}_6$ was occurred, as obtained for the decreasing of Γ values for Fe^{II} atoms.

The δ values of 1.13 or $1.14 (\pm 0.01) \text{ mm s}^{-1}$ obtained for the outer doublet in $0.5\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$, $\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ and $1.5\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glasses (Fig. 1) reflect the presence of $\text{Fe}^{\text{II}}\text{O}_6$ octahedra. Inner doublet of these glasses has δ values of 0.34 – $0.38 (\pm 0.01) \text{ mm s}^{-1}$, reflecting the presence of $\text{Fe}^{\text{III}}\text{O}_4$ tetrahedra. A gradual decrease of Δ was observed from 1.21 to $0.99 (\pm 0.02) \text{ mm s}^{-1}$, indicating that local distortion of $\text{Fe}^{\text{III}}\text{O}_4$ tetrahedra was decreased with an increasing Li_2O content.

DTA curves of $x\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ ($x = 0, 0.5, 1.0$ and 1.5) glasses are shown in **Fig. 2**. The values of T_g were decreased from 503 to 467 , 429 and 404°C when the Li_2O content was increased from 0 to 0.5 , 1.0 , and $1.5 \text{ mol\%}$, respectively. This result is consistent with the decrease with A as observed with Mössbauer spectra.

The ^{57}Fe Mössbauer spectra of $x\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ ($x = 0, 0.5, 1.0$ and 1.5) glasses are illustrated in **Fig. 3**, which param-

Table 1. Mössbauer Parameters for $x\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ ($x = 0, 0.5, 1.0$ and 1.5) Glasses

Sample	$\delta (\text{mm s}^{-1})$	$\Delta (\text{mm s}^{-1})$	$\Gamma (\text{mm s}^{-1})$	$A (\%)$	Species
$x = 0$	0.39 ± 0.01	1.21 ± 0.02	0.52	21.9	Fe^{III}
	1.14	2.20	0.73	78.1	Fe^{II}
$x = 0.5$	0.34	1.13	0.51	40.4	Fe^{III}
	1.14	2.15	0.62	59.6	Fe^{II}
$x = 1.0$	0.36	1.08	0.54	44.1	Fe^{III}
	1.13	2.12	0.60	55.9	Fe^{II}
$x = 1.5$	0.38	0.99	0.54	48.5	Fe^{III}
	1.13	2.12	0.59	51.5	Fe^{II}

Fig. 2. DTA curves of $x\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ ($x = 0, 0.5, 1.0$ and 1.5) glasses. The dashed and crossed lines indicate the glass transition temperature (T_g).

Fig. 3. Mössbauer spectra of $x\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ ($x = 0, 0.5, 1.0$ and 1.5) glasses measured at room temperature.

ters are summarized in **Table 2**. A decrease in the A for Fe^{II} was observed from 78.4% to 59.7%, 56.4%, and 41.9% (Table 2), as also observed in $x\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glasses. A decrease in the Γ values from 0.73 to 0.55 mm s^{-1} was observed for Fe^{II} in $x\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glasses. These Γ values indicate that all the Fe^{II} atoms form a glassy phase. This is also the case for Fe^{III} atoms of which Γ values were estimated to be 0.52 or 0.59 mm s^{-1} . The δ values for Fe^{II} were in a range of 1.12–1.16 (± 0.01) mm s^{-1} , indicating the presence of $\text{Fe}^{\text{II}}\text{O}_6$ octahedra. The other doublet has δ values of 0.38 or 0.39 (± 0.01) mm s^{-1} , which reflects $\text{Fe}^{\text{III}}\text{O}_4$ tetrahedra or $\text{Fe}^{\text{III}}\text{O}_6$ octahedra. A gradual decrease in the Δ value was observed for Fe^{III} from 1.21 to 0.97

Table 2. Mössbauer Parameters for $x\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ ($x = 0, 0.5, 1.0$ and 1.5) Glasses

Sample	δ (mm s^{-1})	Δ (mm s^{-1})	Γ (mm s^{-1})	A (%)	Species
$x = 0$	0.39 ± 0.01	1.21 ± 0.02	0.52	21.9	Fe^{III}
	1.14	2.20	0.73	78.1	Fe^{II}
$x = 0.5$	0.39	1.10	0.59	40.3	Fe^{III}
	1.12	2.12	0.60	59.7	Fe^{II}
$x = 1.0$	0.38	1.01	0.59	43.6	Fe^{III}
	1.16	2.08	0.63	56.4	Fe^{II}
$x = 1.5$	0.39	0.97	0.59	58.1	Fe^{III}
	1.13	2.05	0.55	41.9	Fe^{II}

(± 0.02) mm s^{-1} , indicating that the local dication of $\text{Fe}^{\text{III}}\text{O}_4$ tetrahedra or $\text{Fe}^{\text{II}}\text{O}_6$ octahedra was decreased with an Na_2O content in $x\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glasses. A decrease in the Δ value from 2.20 to 2.05 mm s^{-1} was observed for Fe^{II} in these glasses (Table 2).

DTA curves of $x\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ ($x = 0, 0.5, 1.0$ and 1.5) glasses are shown in **Fig. 4**. Value of T_g was decreased from 503 to 468, 446 and 410°C when the Na_2O content was increased from 0 to 0.5, 1.0 and 1.5 mol%, respectively. This result suggests that the heat resistivity was decreased with a formation of NBO, as reported in several oxide glasses so far.^{7)–12)}

As shown in **Fig. 5**, there observed a linear relationship between T_g and Δ of Fe^{III} in $x\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ ($x = 0, 0.5, 1$ and 1.5) glasses. This linear relationship suggests that the slope of $460^\circ\text{C} (\text{mm s}^{-1})^{-1}$ is intermediate between $680^\circ\text{C} (\text{mm s}^{-1})^{-1}$, which is usually observed when Fe^{III} atoms occupy tetrahedral NWF sites,^{7)–10)} and $260^\circ\text{C} (\text{mm s}^{-1})^{-1}$ which is observed when Fe^{III} atoms occupy octahedral NWF sites.^{7),8)} A linear relationship was also observed when between T_g and Δ of Fe^{III} in $x\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ ($x = 0, 0.5, 1.0$ and 1.5) glasses, as shown in **Fig. 6**. In this case, slope of the straight line of $370^\circ\text{C} (\text{mm s}^{-1})^{-1}$ was also intermediate between 680 (tetrahedral NWF) and $260^\circ\text{C} (\text{mm s}^{-1})^{-1}$ (octahedral NWF).

Fig. 4. DTA curves of $x\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ ($x = 0, 0.5, 1.0$ and 1.5) glasses. The dashed and crossed lines indicate the glass transition temperature (T_g).

Fig. 5. A linear relationship between the glass transition temperature (T_g) and the quadrupole splitting (Δ) of Fe^{III} obtained for $x\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ ($x = 0, 0.5, 1.0$ and 1.5) glasses.

Fig. 6. A linear relationship between the glass transition temperature (T_g) and the quadrupole splitting (Δ) of Fe^{III} obtained for $x\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ ($x = 0, 0.5, 1.0$ and 1.5) glasses.

The electric conductivity, σ , measured by a dc four-probe method at room temperature was evaluated to be $1.3 \times 10^{-6} \text{ S cm}^{-1}$ in $2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glass. In the case of Li_2O -containing compounds, the σ was increased from 2.8×10^{-6} to 7.4×10^{-5} and $1.7 \times 10^{-6} \text{ S cm}^{-1}$ in $0.5\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$, $\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ and $1.5\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glasses, respectively. The σ of Na_2O -containing compounds was increased from 4.3×10^{-6} to 3.1×10^{-5} and $1.0 \times 10^{-6} \text{ S cm}^{-1}$ in $0.5\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$, $\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ and $1.5\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glasses, respectively. The values of electric conductivities of LiFePO_4 compounds at room temperature are in the same order of 10^{-9} – $10^{-10} \text{ S cm}^{-1}$ is generally given in recent literature.^{14,15} Although, the electric conductivity of the order of about 10^{-5} to $10^{-7} \text{ S cm}^{-1}$, is known to be due to a semiconductivity with the electron hopping from V^{IV} to V^{V} in the several vanadate glasses.⁶⁾

4. Conclusions

The ^{57}Fe Mössbauer spectra of $x\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ and $x\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ ($x = 0, 0.5, 1.0$ and 1.5) glasses were utilized for determining the local structure and the occupation of Fe^{III} and Fe^{II} sites. The δ values of these glasses indicate that Fe^{III} atoms form $\text{Fe}^{\text{III}}\text{O}_4$ tetrahedra and $\text{Fe}^{\text{III}}\text{O}_6$ octahedra, whereas Fe^{II} atoms form only $\text{Fe}^{\text{II}}\text{O}_6$ octahedra.

The absorption area for Fe^{II} atoms decreases with an increasing alkali-oxide content. It is considered that an increasing the

alkali-oxide content causes a formation of NBO, such as $\equiv \text{P}-\text{O}^-$ and $\equiv \text{V}-\text{O}^-$.

Slopes of the straight line in T_g - Δ rule were estimated to be 460 and $370^\circ\text{C} (\text{mm s}^{-1})^{-1}$ in $x\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ and $x\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ ($x = 0, 0.5, 1.0$ and 1.5) glasses, respectively. These values are intermediate between $680^\circ\text{C} (\text{mm s}^{-1})^{-1}$, which indicates that Fe^{III} atoms occupy tetrahedral NWF sites, and $260^\circ\text{C} (\text{mm s}^{-1})^{-1}$ reflects that indicates Fe^{III} atoms occupy octahedral NWF sites in $x\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ and $x\text{Na}_2\text{O} \cdot 2\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ glasses.

The electric conductivity obtained by dc four-probe method was of the order of 10^{-5} to $10^{-6} \text{ S cm}^{-1}$.

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