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Correlation of electrical properties and internal friction in mixed conduction glasses containing ionic and electronic conduction (1) Fe_2O_3–Na_2O–P_2O_5 glasses

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The electrical properties and internal friction in $(40 - x)Fe_2O_3 . xNa_2O.60P_2O_5$ glasses were measured. Two or three peak on internal friction were observed in the temperature range of −100 to 300° C at a frequency of about 1 Hz. The peak area of internal friction could be explained quantitatively by the additivity law of diffusion of Na^+ ion and hopping of electrons which are carriers similar to those of dielectric loss. Activation energy, peak temperature of dielectric loss and internal friction showed almost the same value. Both relaxation phenomena have the same mechanism which is due to the diffusion of Na^+ ion and the hopping of electrons between $Fe^{2+} \rightleftharpoons Fe^{3+}$. The high-temperature peak is assumed to result from the interaction between protons or alkali ions and non-bridging oxygen.

1. Introduction

In a previous report, we found that the hopping theory was not satisfied for the conductivity in the glasses of Fe_2O_3–Na_2O–P_2O_5 with a high iron content [1]. An attempt to interpret this abnormal behaviour has been made by us [1], Evstropev *et al.* [2], Grechanic *et al.* [3] and Trap *et al.* [4] on the compositional dependence of the conductivity. However, the detailed mechanism is not yet clear. To clarify the mechanism of such conductivity, the measurement of dielectric relaxation is useful, as short distance transition of electric charge can be analysed. However, the measurement of dielectric relaxation requires very difficult techniques, especially in the range of ultra low frequency. In contrast, the measurement of internal friction is so easy in this frequency range that the behaviour of electric charge can be directly identified at a frequency of around 1 Hz. In this study, the internal friction and electrical properties in the phosphate glasses containing iron and sodium oxide were measured and a quantitative discussion was attempted. Further examinations were conducted on the correlation between internal friction ($Q^{-1} \times 10^3$) and electrical properties (d.c. conductivity, dielectric properties).

2. Experimental procedure

2.1. Preparation of specimen

Three reagents of Fe_2O_3, Na_2CO_3 and H_3PO_4 were of special high grade. They were blended in a ratio so as to make a composition of $(40 - x)Fe_2O_3 . xNa_2O. 60P_2O_5$ charged in an alumina crucible, calcined and then melted at 1200° C for 2 h. Melted glasses were a diameter of 40 mm and a thickness of 3 to 4 mm. After releasing the strain, the disc-shaped glasses were polished on both sides and three gold electrodes were attached using the vapour deposition process. These were the specimens for the measurement of electric properties. Another type of specimen used for the measurement of internal friction was fibre-shaped with a diameter of 1 mm and a length of 40 mm, and was produced by extracting a quartz rod from the melted glass in the alumina crucible.

2.2. Measurements of d.c. conductivity and dielectric properties

Direct current (d.c.) conductivity was measured by current–voltage method by using a vibrating reed d.c. amplifier and the a.c. conductivity was measured in the frequency range of 30 to 10^6 Hz by means of a transformer bridge. Measuring methods and treatments of measured data were the same as those used previously [5].

2.3. Measurements of internal friction

A counter-suspension type torsion pendulum apparatus was used to measure internal friction [6, 7]. The oscillation was detected by the detection coils, amplified by a differential amplifier, (reed by A–D converter) and recorded on disc after calculating the logalithmic decrement (Δ) and cycle time (T_d) by means of computer.

2.4. Valence analysis of iron

The glass sample was crushed fine enough to pass through a 400 mesh, and a predetermined amount was dissolved in a hot hydrochloric acid (1 + 1) solution. When the pH = 2 of the solution by Na_2COOH (35%) solution and HCl, by a titration with EDTA,

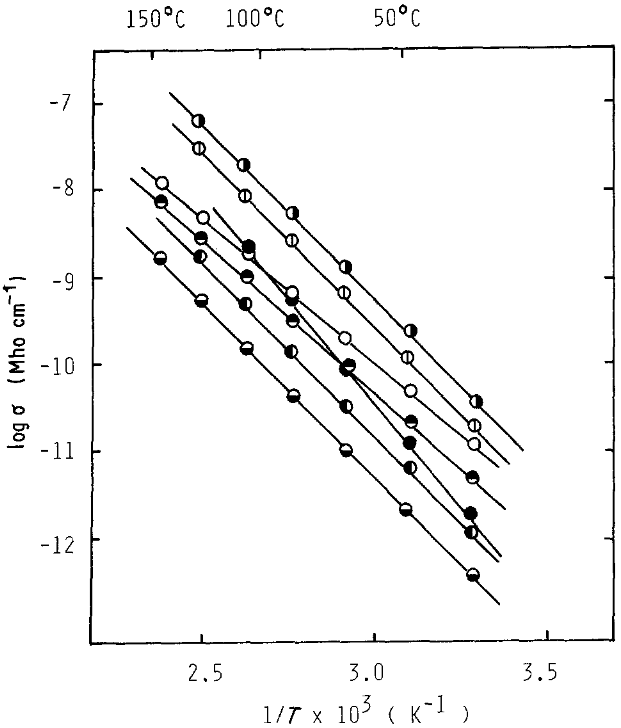

Figure 1 Temperature dependence of log σ in the glasses of $(40 - x)Fe_2O_3 . xNa_2O.60P_2O_5$. (◑) $x = 35$, (⦶) $x = 30$, ○ $x = 0$, ◓ $x = 10$, ● $x = 40$, ◐ $x = 20$, ◒ $x = 15$).

the valence ratio of the iron ion ($R = Fe^{2+}/Fe^{2+} + Fe^{3+}$) was determined. Hereafter, the valence ratio of the iron will be abbreviated to R.

3. Result and discussion

3.1. d.c. conductivity

Direct current polarization was observed for all glasses. As glasses are linear type dielectrics, the conductivity must be calculated from the leakage current, that is the absorption current disappeared perfectly and showed a constant value. Fig. 1 shows the temperature dependence of d.c. conductivity in $(40 - x)Fe_2O_3 . xNa_2O.60P_2O_5$ glasses. All of the specimens satisfied the linear relation. Accordingly, the activation energy for electrical conduction (ΔH_{dc}) can be obtained. The conductivity showed a minimum at $x = 15$ and showed a maximum at $x = 35$.

3.2. Dielectric relaxation

Fig. 2 shows the frequency dependence of both dielectric constant (ε') and dielectric loss (ε'') in $30Fe_2O_3 . 10Na_2O.60P_2O_5$ glasses. The peak position moved toward the higher frequency side with increased temperature and is given by the Equation 1

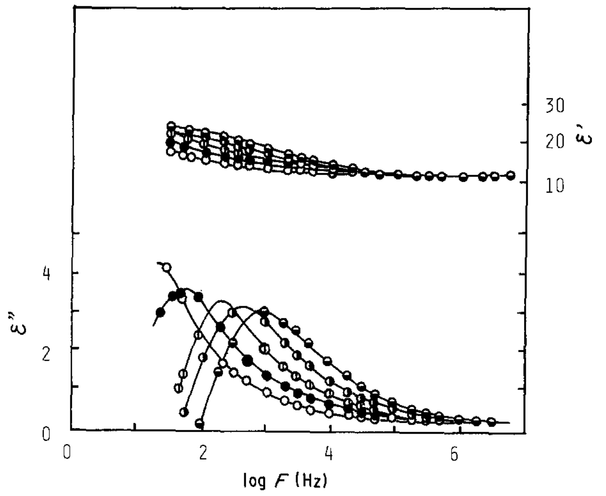

Figure 2 Frequency dependence of ε'' and ε' in the glasses of $30Fe_2O_3 . 10Na_2O.60P_2O_5$ (○ 70° C, ● 90° C, ⦶ 110° C, ◑ 130° C, ◒ 150° C.

$$f = f_{mo} \exp\left(-\frac{\Delta H_{ac}}{RT}\right) \qquad (1)$$

where, ΔH_{ac} is activation energy of dielectric relaxation, f_{mo} is the pre-exponential factor. Table I shows ΔH_{ac} calculated from Equation 1. Both ε' and ε'' showed a minimum at $x = 15$ and a maximum at $x = 35$ similar to d.c. conductivity. The peak temperature at $\log f_{max} = 0$ ($f_{max} = 1$) was obtained from extraporation and is shown in Table I.

3.3. Internal friction

3.3.1. Compositional dependence of internal friction

Figs 3a and b show the temperature dependence of internal friction at 1 Hz frequency in $(40 - x)Fe_2O_3 . xNa_2O.60P_2O_5$ glasses. Two peaks were observed on the low temperature side and the high temperature side at $x = 0$. The low temperature peak separated two peaks with increasing x and the low temperature peak (I) appeared at a lower temperature shifted to the high temperature side. The low temperature peak (II) appearing between the low temperature (I) and high temperature shifted to the low temperature side and the

TABLE I Peak temperature of internal friction, dielectric relaxation and activation energy

x	Peak temp. (1 Hz, °C)				Activation energy (kcal/mol^{-1})				
	Internal friction				Internal friction			ΔH_{ac}	ΔH_{dc}
	Low temp.		High temp.		Low temp.		High temp. ΔH_m		
	I	II			I	II			
0	25		216	21	15.3		23.9	15.6	15.4
5	34	171	244	32	15.6	22.0	24.5	16.3	16.1
10	58	147	259	36	16.3	21.3	25.6	16.7	16.5
15	94		237	55	19.4		22.9	18.0	18.7
20	68		247	40	19.4		23.2	18.3	18.7
25	44		164	36	19.1		21.0	18.8	18.9
30	6		136	23	18.5		20.6	18.8	18.9
35	−23		115	17	18.1		19.7	19.7	19.2
40	–		75	52	–		19.5	23.8	22.4

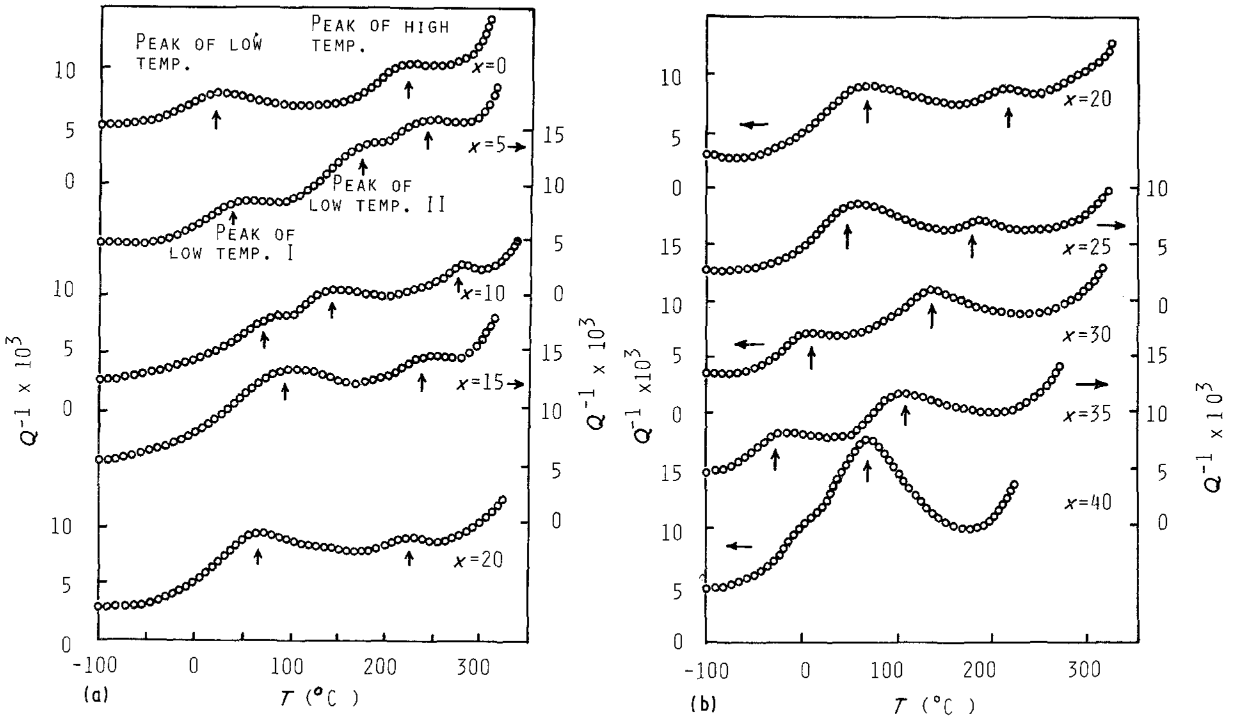

Figure 3 Compositional dependence of Q^{-1} in the glasses of $(40 - x)Fe_2O_3.xNa_2O.60P_2O_5$.

peak was observed at $x = 15$. With increasing x content, the low temperature peak shifted to the low temperature side. On the other hand, the high temperature peak showed a maximum at $x = 10$ and shifted to the low temperature side with increasing x content. The low temperature peak showed a discernible shoulder, at $x = 40$. Table I shows a peak temperature of each composition.

3.3.2. Activation energy of internal friction

Relaxation phenomena occur when a carrier shifts by torsion pendulum, from the outer edge of the specimen. The relaxation time (τ) is given by Equation 1

$$\tau = \tau_0 \exp\left(-\frac{\Delta H_m}{RT}\right) \tag{2}$$

where ΔH_m is the activation energy of internal friction. On the other hand, internal friction is expressed by

$$Q^{-1} = \Delta M \frac{\omega\tau}{1 + (\omega\tau)^2} \tag{3}$$

where ΔM is the intensity of relaxation and ω the angular frequency ($\omega = 2\pi f$). The internal friction satisfies $\omega\tau = 1$ when the peak shows a maximum. Peak temperature changed with measuring frequency. Fig. 4 shows the frequency dependence of internal friction in $10Fe_2O_3 . 30Na_2O.60P_2O_5$ glasses. The peak temperature shifted to the high temperature side with higher frequency. From Equation 2 and $\omega\tau = 1$,

$$\omega\tau = 2\pi f\tau_0 \exp\left(-\frac{\Delta H_m}{RT}\right) \tag{4}$$

$$\ln f = -\ln(2\pi\tau_0) - \frac{\Delta H_m}{RT} \tag{5}$$

The frequency (f_{max}) for the maximum peak and inverse of the corresponding temperature ($1/T$) were found to have a linear relation. The activation energy for internal friction (ΔH_m) was obtained from Equation 5.

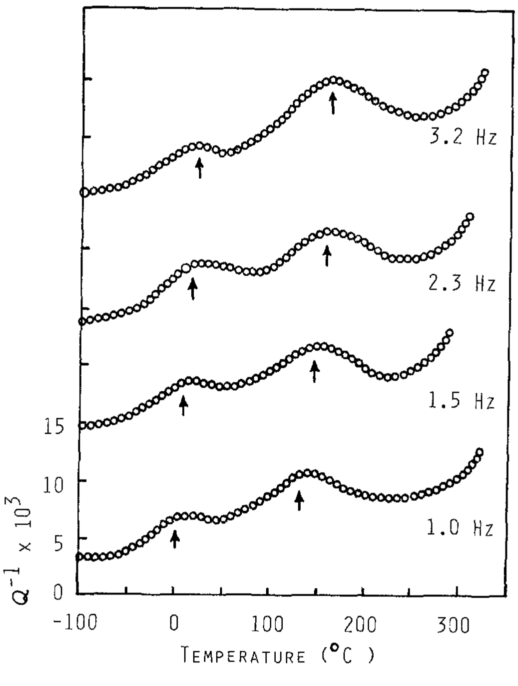

Figure 4 Frequency dependence of Q^{-1} in the glasses of $(40 - x)Fe_2O_3 . 30Na_2O.60P_2O_5$.

3.4. Relation of internal friction peak, d.c. conductivity and dielectric relaxation

3.4.1. Activation energy of low temperature peak, d.c. conductivity and dielectric relaxation

The upper half of Fig. 5 shows the compositional dependence at 1 Hz of low temperature peak on dielectric relaxation and internal friction. The low temperature peak (I) showed a similar tendency to those of dielectric relaxation for all compositions. The lower half of Fig. 5 shows the compositional dependence of activation energy on d.c. conductivity, dielectric relaxation and low temperature peak of internal friction. Activation energy showed an almost similar

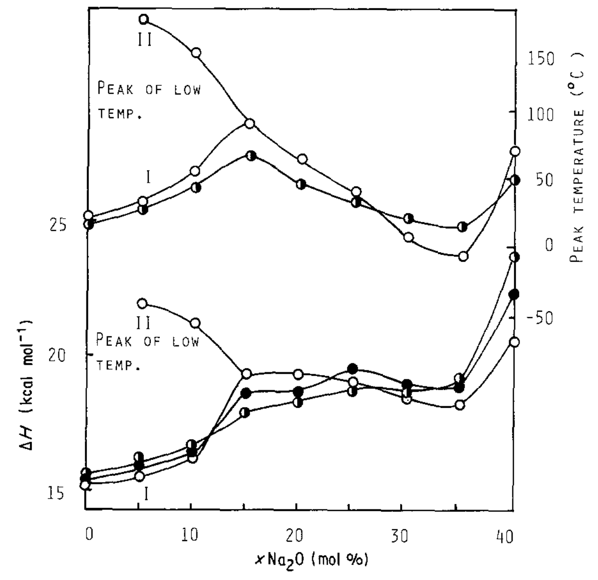

Figure 5 Compositional dependence of activation energy and peak temperature on internal friction in the glasses of $(40 - x)Fe_2O_3 . xNa_2O.60P_2O_5$ (○ peak of low temperature internal friction, ◑ dielectric increment ($\Delta\varepsilon$) ● d.c. conductivity).

tendency. From the above results, it can be seen that the low temperature peak of internal friction is similar to the dielectric relaxation mechanisms which is due to the diffusion of Na^+ ions and hopping of electrons between $Fe^{2+} \rightleftharpoons Fe^{3+}$. The reason why peak (II) of low temperature was not observed for dielectric relaxation is considered to be as follows. The mechanism of dielectric relaxation is considered to be similar to those of internal friction. Therefore the frequency of peak position on dielectric loss (ε'') can be obtained by substituting in Equation 4 the activation energy of the low temperature peak (II) on internal friction. These frequencies were obtained at 0.3 Hz at 150° C for $x = 5$ and 1.4 Hz at 150° C for $x = 10$. However, these values were without the range of measurement for dielectric relaxation.

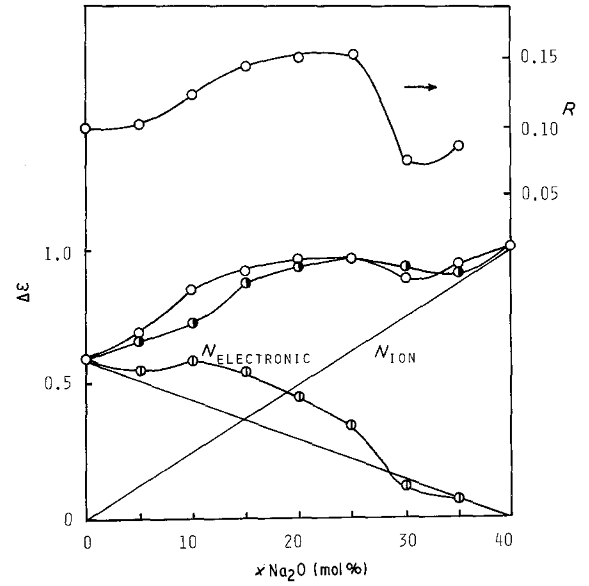

Figure 6 Compositional dependence of R ratio, normalized values of dielectric increment (◑) ($\Delta\varepsilon$) and carrier number (○) in the glasses of $(40 - x)Fe_2O_3 . xNa_2O.60P_2O_5$.

3.4.2. Relation of intensity of dielectric relaxation and carrier number

Fig. 6 shows the compositional dependence of the relative value of $\Delta\varepsilon$ (intensity of dielectric relaxation). $\Delta\varepsilon$ is directly proportional to the carrier number. The relative value of $\Delta\varepsilon$ is that value for which the $x = 40$ is normalized as unity. $\Delta\varepsilon$ was obtained from an area of dielectric loss or $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$, where ε_s is a dielectric constant showing constant value in the low frequency range, ε_∞ is the dielectric constant which shows a constant value in the high frequency range. $\Delta\varepsilon$ are directly proportional to an electric charge or the number of dipole contributing to dielectric relaxation [10]. Total carrier number (N) is obtained by a sum of ionic conduction component (N_{ion}) and electronic conduction component (N_{elec}). The ionic conduction component is directly proportional to the mole number of sodium and electronic conduction components which can be calculated from the concentration of number of carrier ions (Fe^{2+} ion) contained in the glass. Therefore, each carrier number (N) is expressed as follows

$$N = N_{\text{ion}} + N_{\text{elec}} \tag{6}$$

$$N_{\text{ion}} \propto x \tag{7}$$

$$N_{\text{elec}} \propto (40 - x)R \tag{8}$$

where, R is the ratio of Fe^{2+}/Fe (total) calculated from chemical analysis. Fig. 6 shows the compositional dependence of R, electronic conduction component (N_{elec}) by considering the R and the ionic conduction component (N_{ion}). The curve of total carrier number is consistent with the intensity of dielectric relaxation ($\Delta\varepsilon$). This fact shows that the additivity law of diffusion of Na^+ ion and hopping of electrons between $Fe^{2+} \rightleftharpoons Fe^{3+}$ applied for dielectric relaxation phenomena. In this case, the deviation from the calculated value of $\Delta\varepsilon$ near $x = 10$ was considered to be reason that why the peak similar to the low temperature peak (II) could not be measured because of ultra low frequency.

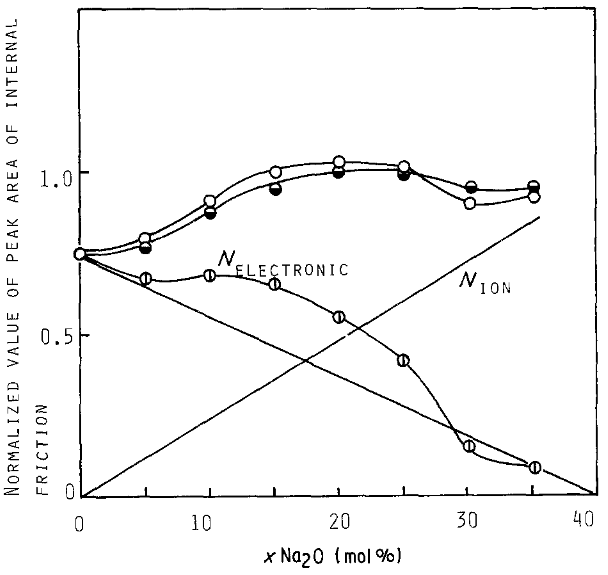

Figure 7 Compositional dependence of carrier number (○) and normalized value of low temperature peak on internal friction (◒) in the glasses of $(40 - x)Fe_2O_3 . xNa_2O.60P_2O_5$.

3.4.3. Relation of peak area of internal friction and carrier number

Fig. 7 shows the compositional dependence of the relative values on the low temperature peak area for internal friction. The relative value is the value when the peak area of $x = 20$ is normalized to unity. The sum of the low temperature peak (I) and peak (II) is the peak area of low temperature for $x = 5$ and $x = 10$. The peak area of internal friction is related to the total carrier number (N) which contribute to internal friction. The total carrier number (N) is expressed in a similar way to that for dielectric relaxation. The calculated value of total carrier number (N) is consistent with the relative value of the low temperature peak area on internal friction. This fact shows the result that the additivity law by diffusion of Na^+ ion and hopping of electrons between $Fe^{2+} \rightleftharpoons Fe^{3+}$ applies for the low temperature peak of internal friction.

3.4.4. Relation between low temperature peak of internal friction and dielectric relaxation

From Section 3.4.1, 3.4.2, and 3.4.3, it is seen that the low temperature peak (I) is related to the hopping between $Fe^{2+} \rightleftharpoons Fe^{3+}$ [6–9] and the low temperature peak (II) is related to the diffusion of Na^+ ions. The low temperature peak above $x = 15$ was considered to the sum of the peaks due to diffusion of Na^+ ions and hopping of electrons as carriers [8].

3.5. Compositional dependence of d.c. conductivity and carrier number

Fig. 8 shows the compositional dependence of d.c. conductivity and activation energy. The compositional dependence of d.c. conductivity showed a minimum at $x = 15$ and a maximum at $x = 35$. An additive conductivity of ionic conduction and electronic conduction, electrical conduction consists of ionic and electronic conduction. Ionic conduction is directly proportional to sodium concentration and electronic conduction follows the hopping theory. The motion of ions and electrons are independent and do not correlate. Therefore, ionic conduction is as follows.

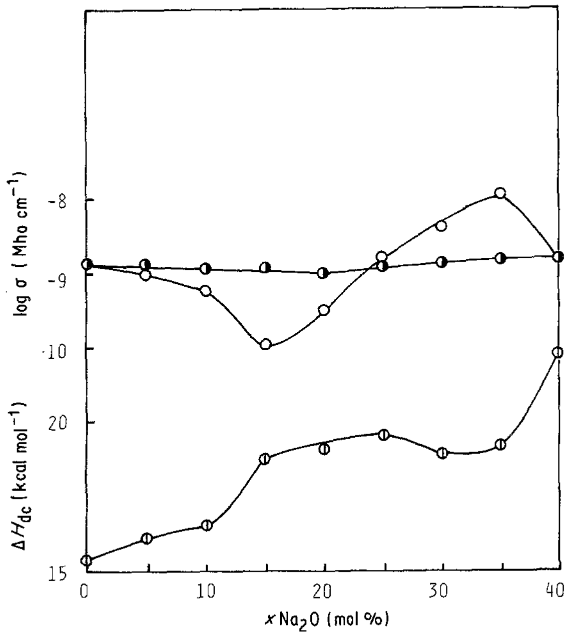

Figure 8 Compositional dependence of log σ (○) and ΔH_{dc} (◐) in the glasses of $(40 - x)Fe_2O_3 . xNa_2O.60P_2O_5$ (◑ additivity law ($\sigma_{ionic} + \sigma_{electronic}$)).

$$\sigma_{ion} = K_1 y e^{-\alpha/RT} \tag{9}$$

where, K_1 is a constant, y is the Na^+ ion concentration, (normalized as 40 mol % Na_2O = 1) and α is the activation energy in the glass of $40Na_2O.60P_2O_5$. On the other hand, electronic conduction is proportional to the number $(1 - y)$ of electrons donors and number $(1 - y)$ of nearest neighbour acceptor around donor.

$$\sigma_{elec} = K_2(1 - y)^2 c(1 - c) e^{-\beta/RT} \tag{10}$$

where, K_2 is a constant, c the ratio of $Fe^{2+}/Fe^{2+} + Fe^{3+}$, and β the activation energy in $40Fe_2O_3 . 60P_2O_5$ glass. From the above results, the additive conductivity is expressed as

$$\sigma = K_1 y e^{-\alpha/RT} + K_2(1 - y)^2 c(1 - c) e^{-\beta/RT} \tag{11}$$

for 100° C, the conductivity of $T = 100°C$ is substituted in Equation 11

$$\sigma_{100°C} = 1.545 \times 10^{-9} xy + 1.441 \times 10^{-8} \times c(1 - c) \tag{12}$$

Fig. 8 shows the calculated values of σ in the $(40 - x)Fe_2O_3 . xNa_2O.60P_2O_5$ glasses. The measured conductivity was smaller than the calculated conductivity. The reason is considered to be as follows. It is well known that Fe^{2+} and Fe^{3+} ions in the phosphate glasses and sodium metaphosphate glasses have a coordination number of 6 [10]. In these circumstances $[Fe^-O_{4/2}]Na^+$ are formed in the glasses [2, 4, 12] and Na^+ ions are trapped. Therefore, ionic conduction is depressed and the hopping conduction is simultaneously depressed with decreasing number of Fe^{3+} ion acceptors. Fig. 9 shows the carrier number of ionic conduction and electronic conduction components obtained from the intensity of dielectric loss ($\Delta\varepsilon$). The

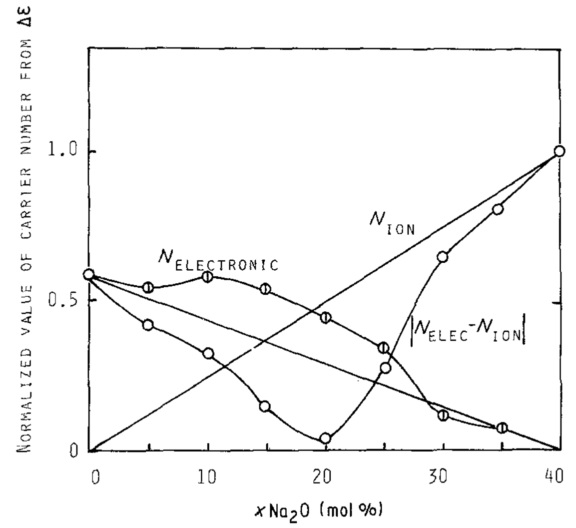

Figure 9 Compositional dependence of carrier number and $|N_{elec} - N_{ion}|$ calculated from $\Delta\varepsilon$ in the glasses of $(40 - x)Fe_2O_3 . xNa_2O.60P_2O_5$.

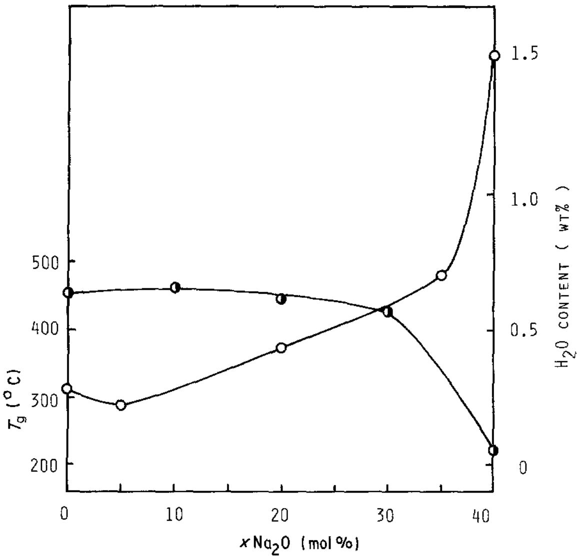

Figure 10 Compositional dependence of T_g (◑) and H_2O content (○) in the glasses of $(40 - x)Fe_2O_3 . xNa_2O.60P_2O_5$.

electronic conduction is predominates at less than $x = 20$ and ionic conduction predominates at more than $x = 20$. Fig. 9 shows the carrier number $|N_{elec} - N_{ion}|$ and the similar tendency to of the measured conductivity. This fact shows the results that the decrease of conductivity near $x = 15$ is due to the decrease the number of carriers by interaction of Na^+ and Fe^{3+} ions. Electronic conduction predominates at less than $x = 10$ and ionic conduction is predominant at more than $x = 15$. The rapid increase of ΔH_{dc} is due to change from electron carrier to ion carrier contributions to the conductivity. The maximum conductivity near $x = 35$ is considered in the following. Fig. 10 shows the glass transition temperature from linear thermal expansion and the water content from chemical analysis. The glass transition temperature for $x = 40$ is low and contains the water of larger quantities. If the water is not contained for $x = 40$, the conductivity may be one order higher. Therefore, the additive conductivity give an almost identical curve in the measured value.

3.6. High temperature peak of internal friction

Fig. 11 shows the compositional dependence of the high temperature peak, activation energy (ΔH_m) and the relative value of peak area for internal friction. It was considered that the high temperature peak was caused by the interaction between the protons or alkali ions and non-bridging oxygen ions [13–16]. From these results, the high temperature peak is considered to the proportional in non-bridging oxygen. The area of the high temperature peak increased with increasing x. This fact shows the amount of the non-bridging oxygen decreases with increasing Fe_2O_3 content and inversely increases with increasing Na_2O content. Furthermore, the amount of non-bridging oxygen increases with increasing water content. Therefore, the amount of non-bridging oxygen is considered to be governed by the Na_2O and water content. The glass structure weakens with increasing amount non- bridging oxygen. Therefore, the activation energy is smaller and the high temperature peak is shifted to the lower temperature side, this is shown in Fig. 11.

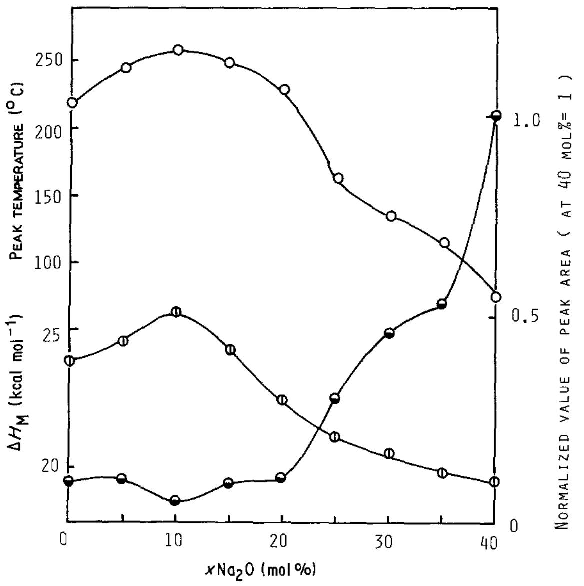

Figure 11 Compositional dependence of activation energy (◐) (ΔH_m), peak temperature (○) and peak area (●) of high temperature on internal friction in the glasses of $(40 - x)Fe_2O_3 . xNa_2O.60P_2O_5$.

4. Conclusion

Electrical properties and internal friction in the $(40 - x)Fe_2O_3 . xNa_2O.60P_2O_5$ glasses were measured and the following results were obtained.

(1) The peak area of dielectric and internal friction could be explained quantitatively by the additivity law of diffusion of Na^+ ion and hopping of electrons which are the carriers.

(2) Activation energy, peak temperature of dielectric relaxation and internal friction showed almost the same value. Both relaxation phenomena have the same mechanism which is due to the diffusion of Na^+ ions and hopping of electrons between $Fe^{2+} \rightleftharpoons Fe^{3+}$.

(3) The conductivity showed a minimum at $x = 15$ and the experimental value showed small values about 1.5 times the calculated value of additive conductivity. It is considered that $[Fe^-O_{4/2}]Na^+$ is formed by the interaction of Na^+ and Fe^{3+} ions and both ions contribute to the conductivity decrease in the glasses.

(4) The high temperature peak is assumed to result from the interaction between protons or alkali ions and non-bridging oxygen. The correlation was found between peak area, peak temperature and activation energy of high temperature.

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