NMR and Raman Studies of $\text{Na}_2\text{O}$–$\text{P}_2\text{O}_5$–$\text{SiO}_2$ Glasses

—Six-Coordinated Si and Basicity—

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$\text{Na}_2\text{O}$–$\text{P}_2\text{O}_5$–$\text{SiO}_2$ ガラスの NMR とラマン分光

—六配位 Si と塩基度との関係—

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The $^{29}\text{Si}$ and $^{31}\text{P}$ nuclear magnetic resonance (NMR) chemical shifts and the $Q_n$ distribution in ternary sodium phosphosilicate glasses were examined. In the $\text{NaPO}_4$–$\text{SiO}_2$ glasses, only the $\text{Si}(Q_6)$ unit from $\text{SiO}_2$ and the $\text{P}(Q_2)$ unit from $\text{NaPO}_4$ are observed. When the $\text{P}_2\text{O}_5$ content increases at fixed mole fractions of $\text{SiO}_2$, the $Q_n$ distribution of $\text{SiO}_2$ changes appreciably due to the formation of 6-coordinated silicon atoms.

Key-words: $\text{Na}_2\text{O}$–$\text{P}_2\text{O}_5$–$\text{SiO}_2$ Glasses, $^{29}\text{Si}$ and $^{31}\text{P}$ NMR, Raman spectra, 6-coordinated Si

1. Introduction

The environment around silicon atoms in glasses is expressed in terms of $\text{SiO}_4$ tetrahedral structural units, $\text{Si}(Q_n)$, where $n$ is the number of bridging oxygen atoms. Analogous to the silica tetrahedron, the PO$_4$ tetrahedron can be expressed by the same structural units. However, one of the phosphorous–oxygen bonds of the PO$_4$ unit is the P=O double bond, so that the P($Q_3$) structural unit is absent in usual alkali phosphate glasses. Magic angle spinning (MAS) NMR techniques have been extensively applied to the structural studies around Si and P in various gels and glasses.1-6 The $\text{Si}(Q_n)$ distribution of binary alkali silicate glasses was studied and the equilibrium constants of the reactions, $2\text{Si}(Q_n) = \text{Si}(Q_{n-1}) + \text{Si}(Q_{n+1}) (n = 1, 2$ and $3)$, were determined.7 The reactions proceed to the right-hand side with a decrease in the ionic radius of the alkali oxides. Thus, the $\text{Si}(Q_n)$ distributions were discussed in terms of the thermodynamic basicity of the alkali silicate melts. In some glasses, the presence of the six-coordinated silicon atoms was observed.8-10 The presence of this structural unit, hereafter denoted by $\text{Si}(Q_6)$, was first observed by means of $^{29}\text{Si}$ NMR of (Na$_2$O–2SiO$_2$)–P$_2$O$_5$ glasses with high P$_2$O$_5$ content. The chemical shift of the NMR of the Si($Q_6$) unit was $-213$ ppm, equal to that of cubic SiP$_2$O$_7$.9

2. Experimental

Although the spin–lattice relaxation time for the Si nucleus in silicate glasses is very long, it can be shortened by spin diffusions from paramagnetic centers. Therefore 0.05 mol% Gd$_2$O$_3$ was added to the batches of starting materials. The materials for producing glass were Na$_2$CO$_3$, NaPO$_4$, NH$_4$H$_2$PO$_4$ and $\text{SiO}_2$. The desired quantities of reagents were thoroughly mixed in acetone. After evaporation of acetone the homogeneously mixed powders were melted in a platinum crucible at $1300^\circ\text{C}$ using an electric furnace and poured into a metal plate. The $^{29}\text{Si}$ and $^{31}\text{P}$ MAS-NMR spectra were obtained by a JEOL JNM-CX300 spectrometer operating at 59.74 and 121.7 MHz, respectively. The thoroughly ground glass powder was loaded into a zirconia spinner tube and spun at 4 to 6.4 kHz. The pulse delay time between 4.5-$\mu$s pulses (a $\pi/2$ pulse) was 5 s. The chemical shift ($\sigma$ in ppm) of $^{29}\text{Si}$ was determined by using polydimethylsilane (PDMS) as a secondary standard. The chemical shift of PDMS was $-34.11$ ppm against tetramethyldisilane, $\sigma = 0$ ppm. When the content of $\text{SiO}_2$ is low, i.e., $5 \text{ mol}\%$, it was necessary to accumulate about 16000 times to obtain meaningful spectra. The spectrum of the $^{31}\text{P}$ NMR was accumulated from 8 to 100 times. The pulse delay time was 10 s. External chemical shift of $^{31}\text{P}$ was $85\%$ H$_3$PO$_4$ aqueous solution. The second standard is hydrogen diammioniumphosphate whose chemical shift is 1.33 ppm from H$_3$PO$_4$. Solution. In the $^{31}\text{P}$ MAS-NMR many side-band peaks appeared. By changing the spinning speed the isotropic peak was determined. All glasses were also characterized by FT–Raman spectroscopy using a JASCO FT–IR 800 with an RPT–800 Raman attachment. The 1064 nm line of a Nd: YAG laser was used as an excitation light source. Laser power was set at 500 mW and 100–300
scans were accumulated with a resolution of 4 cm⁻¹. The compositions of ternary phosphosilicate glasses were shown with glass numbers in Fig. 1. In a composition triangle the series of glasses examined by Dupree et al. are also shown.9)

3. Results

3.1 Sodium silicate and sodium phosphate binary glasses

Figure 2 represents the ²⁹Si NMR spectra of binary sodium silicate glasses. The profiles of the NMR spectra change systematically with composition, which is similar to those reported in previously literature. The NMR spectra of binary sodium silicate glasses consist of the four peaks at around -69, -77, -90 and -100 ppm, which are assigned to the Si(Q1), Si(Q2), Si(Q3) and Si(Q4) units, respectively. The distributions of structural units derived from the peak area of individual components by Gaussian functions are shown in Fig. 3. Dotted lines denote the distribution curves of the individual Si(Qn) structural unit determined by Maekawa et al.2) The present data agree well with the values given in the literature. The ³¹P NMR spectra of binary sodium phosphate glasses are shown in Fig. 4. The ³¹P NMR spectra consist of the three peaks at around 2, -20 and -37 ppm, which are assigned to the P(Q1), P(Q2) and P(Q3) units, respectively. The deconvolution by Gaussian functions can also be applied and the composition dependence of the P(Qn) distributions against Na₂O content can be estimated as shown in Fig. 5. Although the composition dependence of P(Qn) distributions was similar to those seen in silicate glasses, the P(Qn) distributions against composition are sharper compared to the Si(Qn) distribution curves of sodium silicate glasses. Figure 6 shows the Raman spectra of binary sodium phosphate glasses. The Raman spectrum of sodium metaphosphate consists of three peaks around 1270, 1170 and 690 cm⁻¹, that agree with the values reported in the literature. With an increase in Na₂O content, Raman shift around 1170
cm\(^{-1}\) changes slightly to lower wavenumber. New peaks appear around 1010 and 1110 cm\(^{-1}\), whose intensities increase with an increase in Na\(_2\)O content. The peak around 1270 cm\(^{-1}\) shifts slightly to a lower frequency and the peak around 690 cm\(^{-1}\) changes to the higher frequency side with an increase in Na\(_2\)O content.

3.2 Sodium phosphosilicate glasses

3.2.1 \((1-x)[0.5\text{Na}_2\text{O}-0.5\text{P}_2\text{O}_5]-x\text{SiO}_2\) glasses (Series I)

The \(^{29}\text{Si}\) and \(^{31}\text{P}\) NMR spectra of Series I are shown in Figs. 7 (a) and (b). The \(^{29}\text{Si}\) NMR spectra consist of the Si (Q\(_4\)) unit only, whose chemical shifts change to a more positive side with an increase in SiO\(_2\) content. The chemical shifts of \(^{31}\text{P}\) NMR change only slightly to a more positive side with an increase in SiO\(_2\) content. The Raman spectra of the glasses are shown in Fig. 7 (c). Although the peak around 480 cm\(^{-1}\) is found in ternary glasses, the main feature does not change significantly from that seen in sodium metaphosphate glass (glass 11).

3.2.2 \((1-x)[0.4\text{Na}_2\text{O}-0.6\text{P}_2\text{O}_5]-x\text{SiO}_2\) glasses (Series II)

The \(^{29}\text{Si}\) and \(^{31}\text{P}\) NMR spectra of the glasses of Series II are shown in Figs. 8 (a) and (b). In glasses of high SiO\(_2\) content, the signal due to the Si (Q\(_6\)) and the Si (Q\(_4\)) units are observed. On the other hand, in glasses of low SiO\(_2\) content only the signal by the Si (Q\(_6\)) unit is observed (glasses 24 and 25). The spectral features of \(^{31}\text{P}\) NMR do not change much with composition. However, chemical shifts of the P (Q\(_4\)) and the P (Q\(_6\)) units of the PO\(_4\) tetrahedra shift to the positive side with an increase in SiO\(_2\) content.

3.2.3 \(0.95[x\text{Na}_2\text{O}-(1-x)\text{P}_2\text{O}_5]-0.05\text{SiO}_2\) glasses (Series III) and \(0.9[x\text{ Na}_2\text{O}-(1-x)\text{P}_2\text{O}_5]-0.1\text{ SiO}_2\) (Series IV)

The NMR spectra of the glasses of Series III are shown in Figs. 9 (a) and (b). The \(^{29}\text{Si}\) NMR spectra of the glasses show that the Si (Q\(_4\)) and the Si (Q\(_6\)) units coexist when the P\(_2\)O\(_5\) content is low (glass 32). With an increase in the P\(_2\)O\(_5\) content, the Si (Q\(_6\)) unit disappears and the spectra consist of the Si (Q\(_4\)) unit alone. The chemical shift of the Si (Q\(_4\)) unit moves to more negative values and a signal due to the Si (Q\(_6\)) unit appears with further increase in the P\(_2\)O\(_5\) content. The profile of the \(^{31}\text{P}\) NMR spectra with [P\(_2\)O\(_5\)]/[Na\(_2\)O] concentration ratio of Series III does not change much from those seen in the binary sodium phosphate glasses. The \(^{29}\text{Si}\) and \(^{31}\text{P}\) NMR spectra of Series IV are shown in Figs. 10 (a) and (b). In the glasses 33, 34 and 24 only the signal due to the Si (Q\(_6\)) was observed. The composition dependence of the \(^{31}\text{P}\) NMR spectra in Series IV is similar to that of the glasses of Series III as well as of the binary sodium phosphate glasses. The Raman spectra of the glasses of Series III and IV are shown in Figs. 9 (c) and 10 (c). In Series IV the intensities around 1200 and 1350 cm\(^{-1}\) increase with an increase in P\(_2\)O\(_5\) content. The peak intensity around 1000 cm\(^{-1}\) decreases with an increase in P\(_2\)O\(_5\) content.

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Fig. 7. \(^{29}\text{Si}\) (a) and \(^{31}\text{P}\) (b) NMR and Raman (c) spectra of \((1-x)[0.5\text{Na}_2\text{O}-0.5\text{P}_2\text{O}_5]-x\text{SiO}_2\) glasses (Series I).

Fig. 8. \(^{29}\text{Si}\) (a) and \(^{31}\text{P}\) (b) NMR and Raman (c) spectra of \((1-x)[0.4\text{Na}_2\text{O}-0.6\text{P}_2\text{O}_5]-x\text{SiO}_2\) glasses (Series II).
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Fig. 9. $^{29}$Si (a) and $^{31}$P (b) NMR and Raman (c) spectra of 0.95[$x$Na$_2$O·(1-$x$)P$_2$O$_5$]-0.05SiO$_2$ glasses (Series ‡V).

Fig. 10. $^{29}$Si (a) and $^{31}$P (b) NMR and Raman (c) spectra of 0.9[$x$Na$_2$O·(1-$x$)P$_2$O$_5$]-0.1SiO$_2$ glasses (Series ‡W).

4. Discussion

4.1 Si($Q_n$) and P($Q_n$) distributions of binary glasses and basicities

The Si($Q_n$) distribution of binary alkali silicate glasses was determined by the following equilibrium.

\[ 2\text{Si($Q_n$)} = \text{Si($Q_{n-1}$)} + \text{Si($Q_{n+1}$)} \quad (n=1, 2 \text{ and } 3) \quad (1) \]

The equilibrium was understood in terms of neutralization of the silica network by basic alkali oxides. For example, the equilibrium constants $k_n$ (=[Si($Q_2$)]/[Si($Q_1$)]/[Si ($Q_4$)])$^2$, of the above reaction were determined to be 0.08, 0.02 and 0.01 for Li-, Na- and K-silicate glasses, respectively; thus, the Si($Q_n$) distribution curves against contents of alkali oxide were sharpest in K$_2$O-SiO$_2$.\(^2\) Prow et al. determined the P($Q_n$) distribution of x(Na$_2$O+H$_2$O)-(1-x)P$_2$O$_5$ glasses.\(^5\) The P($Q_n$) distribution could be fitted well by the straight lines when one mole of Na$_2$O or H$_2$O produced two moles of non-bridging oxygens. The lines of the P($Q_n$) distribution in Fig. 5 are the ones where the above idea is applied. This corresponds to the fact that the equilibrium constants of the reaction,

\[ \text{P($Q_n$)} = \text{P($Q_{n-1}$)} + \text{P($Q_{n+1}$)} \quad (n=1 \text{ and } 2) \quad (2) \]

are all zero. The basicities of the oxide melts containing Na$_2$O were evaluated by the thermodynamic activities of Na$_2$O, i.e., $-\log a$(Na$_2$O). The basicities increase in the following order when the concentration of Na$_2$O was fixed.\(^6\)

Na$_2$O-P$_2$O$_5$<Na$_2$O-B$_2$O$_3$<Na$_2$O-SiO$_2$ (3)

Thus, the acidic strength of P$_2$O$_5$ is larger than that of SiO$_2$. Thus, in sodium phosphate glasses the neutralization of the PO$_4$ network proceeds quantitatively with an addition of Na$_2$O to P$_2$O$_5$.

The Raman shift around 1160 cm$^{-1}$, commonly seen in glasses, is due to the symmetric stretching mode of the terminal oxygen, (P($Q_2$) unit), on each tetrahedron. The peak around 1380 cm$^{-1}$ is due to the P=O stretching mode of the P($Q_3$) unit. The relative intensity around 1270 cm$^{-1}$, which is due to the P-O-P stretching vibration of the P($Q_3$) chain. The disappearance of the P($Q_3$)-unit and appearance of the P($Q_1$)-unit in Raman spectra of binary sodium phosphate glasses support the $^{31}$P NMR spectra.

4.2 Alkali phosphosilicate glasses

4.2.1 Series I

The basicities of SiO$_2$, if defined, may be estimated by an extrapolation of the pO values of the binary sodium silicate melts\(^7\) to zero content of Na$_2$O, which yields a value almost equal to that of sodium metaphosphate. The glasses of Series I may be considered to be the mixtures of the two
glasses of the same basicities such as SiO2 and NaPO3. Thus the basicity does not change among glasses in Series I, so it is expected that the Si(Q6) of SiO2 and the P(Q4) of NaPO3 mix randomly. In effect, the 29Si NMR and 31P NMR consist of the Si(Q6) and the P(Q4) structural units, respectively. With an increase in the P2O5 content the number of the Si-O-P bonds increases. Because the electronegative phosphorous atoms attach to the SiO2 tetrahedron, the chemical shift of the 29Si NMR becomes more negative. The Raman shift around 480 cm-1 is assigned to the Si-Q-Si bend mode, whose intensities increase with an increase in SiO2 content.

4.2.2 Series II
In this series, the formation of Si(Q6) can be expected, because the basicity of 40Na2O-60P2O5 glass is lower than that of SiO2. When the basicities of the glasses become lower than that of SiO2, SiO2 behaves as if it were a basic oxide and the Si(Q6) unit may be formed. The 31P NMR spectra do not change from that of binary sodium phosphate glass without the chemical shift in each component. Dupree et al.20 showed that an increase in population of the Si(Q6) results in an increase in intensity of -33 ppm peak of 31P NMR spectra in phospho-alumino-silicate glasses. This peak corresponds to the P(Q4) unit whose P-O bonds are all bridging type. The presence of the P(Q4) unit in the alkali phosphosilicate glasses, if present, cannot be clearly differentiated from the 31P NMR spectra (Fig. 8(b)), because the peak around -38 ppm due to P(Q1) overlap and deconvolution of the spectra could not quantitatively be made.

4.2.3 Series III and IV
The introduction of P2O5 to K2O (or Na2O)-SiO2 glasses removed the alkali ions with low n from the Si(Qn) units and repolymerized the silicate network.20,21 At the same time, the concentration of the PO4 units with low n numbers increased. This phenomenon can be explained by the fact that the acid strength of P2O5 to Na2O is stronger than that of SiO2. The disappearance of the Si(Q6) unit in Series III (Fig. 9(a)) can be explained by this difference of the acid strength between P2O5 and SiO2. The chemical shift of the Si(Q6) units in Series III and IV moves to the negative side with an increase in P2O5. This is due to the formation of the Si-O-P bond. The chemical shifts of the Si(Q6) unit assume more negative values because the electronegative phosphorous atoms attach to the SiO2 tetrahedron. The fraction of Si(Q6) increases with a decrease in basicity, i.e., the [Si(Q6)]/[Si(Qn)] ratio increases with a decrease in the SiO2 concentration.

4.3 Correlation between NMR and Raman spectra
The peaks around 1200 and 1350 cm-1 appeared in glasses with the Si(Q6) structural unit. The Raman spectra around 1100 to 1200 cm-1 could be deconvoluted into three Lorentzian functions (see Fig. 10(c), arrow 1100, 1160 and 1200 cm-1). Among them, the peak at 1160 cm-1 is assigned to the PO4- chain unit (P(Q4) unit) and the peak at 1100 cm-1 is assigned to that of the P(Q2) unit, pyrophosphate P2O74- dieter. Figure 11 represents the relationship between the [Si(Q6)]/[Si(Q4)] ratio from the 29Si NMR spectra and area ratio of two peaks, R = S(1200 cm-1)/S(1100 cm-1). A good correlation between the two values is observed. However, at present it is not clear whether or not the peak around 1200 cm-1 corresponds to the P(Q4) unit whose P-O bonds are all bridging type.

4.4 Optical basicity
Figure 12 represents the correlation between the optical basicity17 and the population of the Si(Q6) unit in glasses. The population of Si(Q6) increased abruptly when the optical basicities decreased beyond about 0.48, i.e., the optical basicity of SiO2 glass. In this figure the data cited in the literature9),11),14) are also shown. In each system, the population the Si(Q6) also increased with a decrease in optical basicities. However, the population–optical basicity curves differ from each other. This largely depends on the content of SiO2 in glasses.

5. Conclusions
The structural units, Si(Q6) and P(Q4), in ternary sodium phosphosilicate glasses were examined by means of the MAS-NMR and Raman spectra. By the formation of Si–O–P bonds the 29Si and the 31P chemical shifts move to the more negative and positive side, respectively. When the P2O5 content increases at the fixed molar fraction of SiO2 equal to 0.1 and 0.05, the Si(Q6) unit appeared. It is expected that the Si(Q6) unit should be formed in the glasses whose composition is P2O5-rich range from the line connecting SiO2 and sodium metaphosphate in a composition diagram. The appearance of Si(Q6) as well as the change of the Si(Q6) and the P(Q4) distributions can be understood by the relative acidic strengths of SiO2 and P2O5.

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