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Structure and formation mechanism of six-fold coordinated silicon in phosphosilicate glasses

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The local structure of sixfold oxygen coordinated silicon ($^{[6]}$Si) in sodium phosphosilicate glasses has been investigated using MAS NMR spectroscopy and *ab initio* quantum-chemical techniques. It has been demonstrated that $^{[6]}$Si is interconnected by six PO_4 tetrahedral units by sharing only their corners, forming a nearly regular $[SiO_{6/2}]^{2-}$ octahedral site. Alkali cations behave as charge compensators of the doubly charged $^{[6]}$Si species and hence play an indispensable role in stabilizing the peculiar octahedral coordination in the glasses.

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It has generally been accepted that fourfold coordinated silicon ($^{[6]}$Si) is the basic building block of silica-based glasses, as postulated by Zachariasen in 1932.[1] Zachariasen[1] has argued against sixfold coordination in glasses because it would force periodicity on the lattice and eventually disrupt the vitreous state. However, a pioneering magic angle spinning (MAS) nuclear magnetic resonance (NMR) study by Dupree, Holland, and Mortuza[2] have shown that sixfold coordinated Si ($^{[6]}$Si) does exist in some sodium phosphosilicate glasses even at ambient pressures. In pure SiO_2 glass, an increase in the coordination number of Si has only been observed under high pressures over ∼10 GPa.[3] As P_2O_5 content increased in a series of R_2O-P_2O_5-SiO_2 glasses (R=Li, Na, K), Dupree *et al.*[2,4,5] observed the appearance of a ^{29}Si signal with a chemical shift of −213 ppm, which is located well beyond the range of chemical shifts for the tetrahedral Si species (−70–−110 ppm) but within a range for $^{[6]}$Si species observed for crystalline compounds such as stishovite, a high-pressure SiO_2 polymorph, and SiP_2O_7 (−194–−214 ppm).[6–8] Subsequent ^{29}Si MAS NMR studies by other researchers have demonstrated that $^{[6]}$Si can be detected in other phosphosilicate glasses, for example, MO-P_2O_5-SiO_2 (M=Mg, Ca, Sr, Ba, Cd) glasses.[9–11]

On the basis of the experimental results, Dupree *et al.*[2,12] suggested the following as for the structural nature of $^{[6]}$Si in glasses: (1) unlike those in crystalline systems, alkali (and/or alkali earth) cations in glasses most likely play an important role in stabilizing the $^{[6]}$Si unit and (2) the resulting basic structural environment of the $^{[6]}$Si in these glasses is well defined but is different, or rather less distorted, than that in the crystals. To our knowledge, however, there has been no accepted structural model or the formation mechanism of the $^{[6]}$Si sites in phosphosilicate glasses. To clarify the microscopic coordination environment of $^{[6]}$Si in glasses, we here perform a series of quantitative ^{29}Si and ^{31}P MAS NMR investigations on Na_2O-P_2O_5-SiO_2 glasses along with *ab initio* quantum-chemical calculations using clusters of atoms modeling the local structure of the corresponding glasses.

Glasses in compositions $a\mathrm{Na_2O}\cdot b\mathrm{P_2O_5}\cdot c\mathrm{SiO_2}$ were prepared from analytical grade SiO_2, Na_2CO_3, and $NH_4H_2PO_4$, which was preheated at 200 °C to volatilize NH_3 and H_2O. The mixture of powders was heated in a Pt crucible at 1100 °C for 1 h. The melt was quenched by squashing between two stainless steel plates to obtain a homogeneous glass. For each composition, an additional 0.05–0.1 mol % $MnCO_3$ was added to reduce the ^{29}Si NMR relaxation time. To evaluate the effect of the addition of SiO_2 on the (de)polymerization of the phosphate network, we fixed the nominal ratio $P_2O_5/Na_2O=1.6$ in preparing this series of glasses. As will be shown below, the amount of SiO_2 was so chosen as to include only $^{[6]}$Si as Si species in the resultant glass samples. The elemental analysis was performed with a Rigaku ZSX x-ray fluorescence spectrometer. The analyzed compositions of the samples NP1 and NPS1-4, are shown in Table I. ^{29}Si and ^{31}P MAS NMR spectra were recorded on a Chemagnetics CMX 400 spectrometer. The ^{29}Si MAS NMR signals were obtained at 79.4 MHz using 4.0 μs pulses followed by a delay of 30 s and a 3.5 kHz spinning rate, whereas a higher rotational rate of 14 kHz, a 161.9 MHz resonance frequency, 3 μs pulses with a 15 s delay were used for ^{31}P nuclei. The chemical shifts of ^{29}Si and ^{31}P were measured relative to tetramethylsilane (TMS) and an 80% solution of H_3PO_4, respectively.

Figure 1 shows the ^{29}Si MAS NMR spectra of the sodium phosphosilicate glasses, NPS1-4. It is clear from Fig. 1 that all the ^{29}Si spectra contain a single resonance at ∼−213 ppm, which is attributed to $^{[6]}$Si, although a very faint peak at ∼−120 ppm characteristic of Si(Q^4) begins to emerge with increasing Si content; in the Q^n nomenclature,

TABLE I. Analyzed compositions (mol %) and structural parameters for the glasses studied.

Sample	Na_2O	P_2O_5	SiO_2	P_2O_5/Na_2O	f_{ideal} [P(Q^3)][a]	f_{exp} [P(Q^3)][b]	R[c]
NP1	38.4	61.6	0	1.60	37.6	37.2	
NPS1	37.4	60.6	2.0	1.62	38.3	40.6	1.4
NPS2	36.3	58.7	5.0	1.62	38.1	48.9	2.5
NPS3	34.6	57.4	8.0	1.66	39.7	54.3	2.1
NPS4	34.5	55.5	10.0	1.61	37.8	57.2	2.1

[a] Fraction of P(Q^3) determined by analyzed compositions and Eq. (1).

[b] Fraction of P(Q^3) determined by line fit analysis of the ^{31}P MAS NMR spectra.

[c] The values were obtained by Eq. (2).

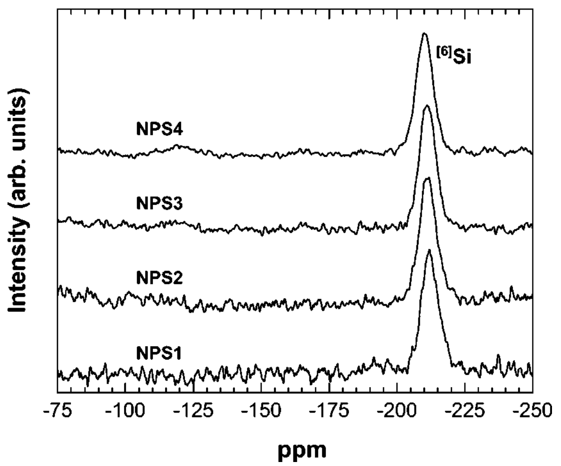

FIG. 1. ^{29}Si MAS NMR spectra of compositions NPS1, NPS2, NPS3, and NPS4.

the value of n is equal to the number of bridging oxygens on a given tetrahedral unit. It is hence quite likely that all Si atoms are virtually in sixfold coordination in these glasses. That is, in the present samples, the glass network consists solely of $^{[6]}$Si and fourfold coordinated P(Q^n) species. On the other hand, the ^{31}P spectra shown in Fig. 2 are composed of two peaks at ~ -25 and ~ -38 ppm, which are attributed to P(Q^2) and P(Q^3) species, respectively.[13] The intensity of P(Q^3) relative to that of P(Q^2) increases with increasing SiO$_2$ content. We also see from Fig. 2 that the position of P(Q^3) shows a more positive shift than that of P(Q^2) with increasing Si content, indicating that the formation of $^{[6]}$Si can change the P environment especially of P(Q^3).

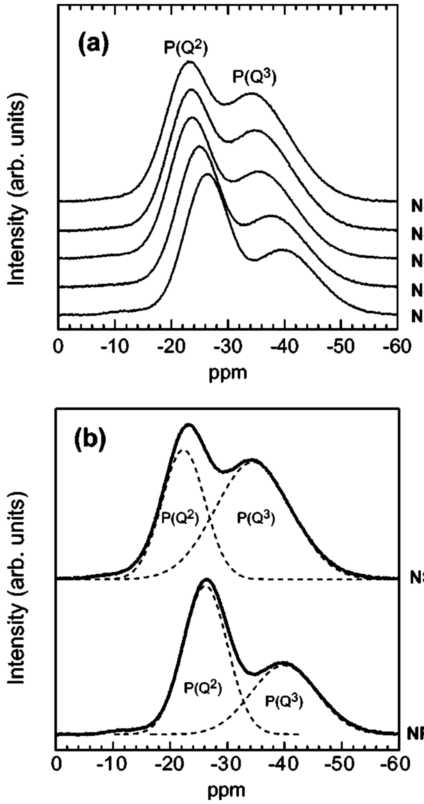

FIG. 2. (a) ^{31}P MAS NMR spectra of compositions PS1, NPS1, NPS2, NPS3, and NPS4. (b) Examples of the decomposition of the spectra into two Gaussian components (broken lines) are shown.

On the basis of the above experimental results, we then discuss the formation mechanism of $^{[6]}$Si in these glassy systems. In pure P$_2$O$_5$ glass, the basic building block is the P(Q^3) tetrahedron, possessing three bridging oxygens and one terminal double-bonded oxygen.[14] The addition of a modifying oxide R_2O results in the creation of nonbridging oxygens at the expense of bridging oxygens, causing the depolymerization reaction of the phosphate network as follows: $2\mathrm{P}(Q^3)+R_2\mathrm{O}\rightarrow 2\mathrm{P}(Q^2)$.[14] Thus, in the ultraphosphate region ($a \leqslant b$ for $aR_2\mathrm{O}\cdot b\mathrm{P}_2\mathrm{O}_5$ glasses), the fraction of P(Q^3) units are ideally given by

$$f_{\mathrm{ideal}}[\mathrm{P}(Q^3)] = \frac{b-a}{b}. \quad (1)$$

The calculated values of $f_{\mathrm{ideal}}[\mathrm{P}(Q^3)]$ estimated from the analyzed Na$_2$O and P$_2$O$_5$ compositions of the glasses are shown in Table I. In Table I, we also show the values of $f_{\mathrm{exp}}[\mathrm{P}(Q^3)]$, which were obtained from the decomposition of the observed ^{31}P MAS NMR line shapes into two Gaussian components [see Fig. 2(b)]. As for the glass NP1, we see a good agreement between $f_{\mathrm{ideal}}[\mathrm{P}(Q^3)]$ and $f_{\mathrm{exp}}[\mathrm{P}(Q^3)]$, indicating that this binary prediction can be applied to the P(Q^n) distributions in sodium phosphate systems, as has already been confirmed by previous researchers.[15] Table I, however, reveals that the addition of small amounts of SiO$_2$ results in an appreciable deviation from the prediction represented by Eq. (1); the difference between $f_{\mathrm{ideal}}[\mathrm{P}(Q^3)]$ and $f_{\mathrm{exp}}[\mathrm{P}(Q^3)]$ increases with increasing SiO$_2$ content. This deviation certainly results from the incorporation of octahedral Si species into the phosphate network since, as mentioned earlier, all Si atoms in the glasses are virtually present as $^{[6]}$Si. It is hence most likely that the addition of SiO$_2$ contributes to the conversion of P(Q^2) to P(Q^3) as long as the added Si atoms exist as $^{[6]}$Si species. According to the previous two-dimensional shift correlated (COSY) ^{29}Si MAS NMR studies on sodium phosphosilicate glasses,[16] each $^{[6]}$Si site is expected to be linked by phosphorus tetrahedra at the nearest neighbor level; that is, $^{[4]}$P-O-$^{[6]}$Si linkages are formed in the phosphosilicate glass network. Judging from all these experimental results, we propose that the formation process of $^{[6]}$Si can be viewed as the bonding of nonbridging oxygens of P(Q^2) to $^{[4]}$Si species, followed by the repolymerization of the glass network to form P(Q^3)-O-$^{[6]}$Si linkages. As mentioned previously, the position of the P(Q^3) peak is more affected, or less shielded, than that of the P(Q^2) peak with increasing SiO$_2$ content. The decreased shielding at the P(Q^3) nucleus is indicative of the presence of Si, rather than P, in its nearest neighbor site, in harmony with the scheme assuming the formation of the P(Q^3)-O-$^{[6]}$Si linkages.

Then, the point is how many P(Q^2) species are bonded to each $^{[4]}$Si to form one $^{[6]}$Si unit. To clarify this, we calculated the following conversion ratio R for glasses having the composition $a\mathrm{Na}_2\mathrm{O}\cdot b\mathrm{P}_2\mathrm{O}_5\cdot c\mathrm{SiO}_2$:

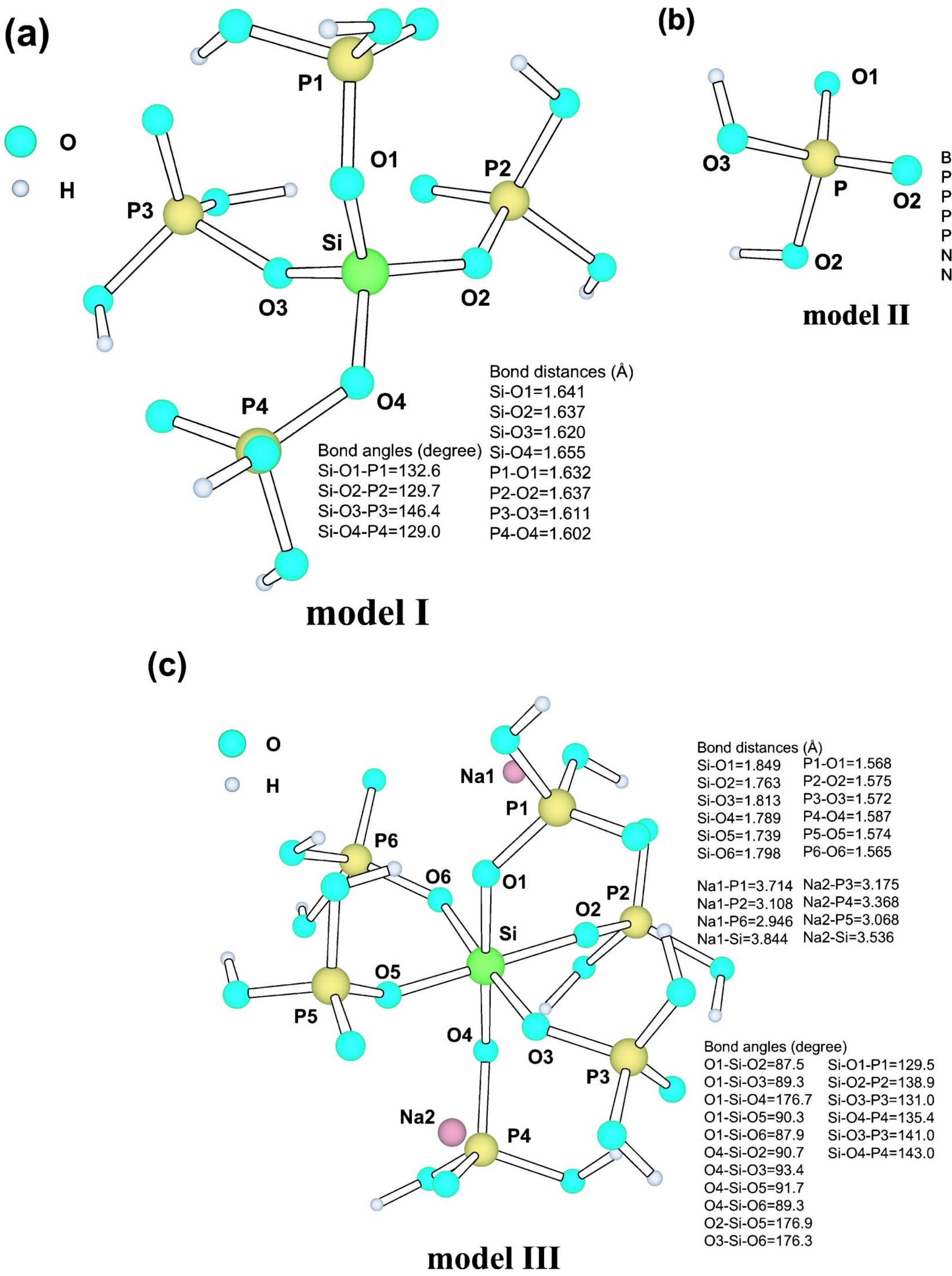

FIG. 3. (Color online) Clusters of atoms used to model the local structure of (a) Si(Q^4) (model I) and (b) P(Q^2) (model II) and (c) a complex cluster consisting of one model I and two model II clusters (model III). The geometry of the clusters was optimized at the B3LYP/6-31G(d) level. Principal optimized bond distances and angles are shown. H atoms are used to terminate "surface" oxygen atoms of the respective clusters.

$$R = \frac{2b\{f_{\mathrm{ideal}}[\mathrm{P}(Q^3)] - f_{\mathrm{exp}}[\mathrm{P}(Q^3)]\}}{c}. \qquad (2)$$

The ratio R corresponds to the number of converted tetrahedral P units from P(Q^2) to P(Q^3) per each $^{[6]}$Si unit. The R values calculated for the glasses NPS 1-4 are listed in Table I. One sees from Table I that the ratio R is ~2 irrespective of the amount of SiO$_2$ incorporated into the phosphate network. This result elucidates that one $^{[6]}$Si unit is formed as a result of the interaction between two P(Q^2) and one $^{[4]}$Si units. Thus, we can conclude that $^{[6]}$Si is created through the reaction

$$^{[4]}\mathrm{Si} + 2\mathrm{P}(Q^2) \rightarrow \mathrm{P}(Q^3) - {}^{[6]}\mathrm{Si} - \mathrm{P}(Q^3). \qquad (3)$$

To evaluate the local coordination environment of thus formed $^{[6]}$Si species, we have performed *ab initio* quantum-chemical calculations on clusters of atoms[17,18] modeling the respective Si and P species involved in the above reaction. Figure 3 shows the clusters of atoms used to model $^{[4]}$Si (model I) and P(Q^2) (model II) species. In the clusters, the surface oxygen atoms have been terminated by H atoms.[17,18] We next combined these clusters (one model I and two model II clusters) and obtained its optimized geometry to investigate whether the $^{[6]}$Si species predicted by Eq. (3) is energetically realistic or not [model III, see Fig. 3(c)]. Full geometry optimization for the above clusters was performed at the density functional theory (DFT) level with the 6-31G(d) basis set.[19] For the DFT calculations, we used the B3LYP exchange-correlation functional consisting of the Lee-Yang-Parr correlation functional[20] in conjunction with a hybrid exchange functional proposed by Becke.[21] All the DFT calculations in this work were performed using the GAUSSIAN 98 program.[22]

As shown in the optimized geometry of model III, we have found that nonbridging oxygens in P(Q^3) in model II-type clusters are bonded to the central $^{[4]}$Si unit in model I, resulting in a nearly regular "corner-sharing octahedral" Si structure surrounded by six P(Q^3) units. Two of the six P(Q^3) units are derived originally from P(Q^2) units in model II, but we do not see any noticeable structural difference among these surrounding P(Q^3) units. We also see from Fig. 3(c) that two sodium ions behave as charge compensators of the doubly charged $[\mathrm{SiO}_{6/2}]^{2-}$ unit and hence play a vital role in stabilizing the octahedral environment, in accordance with the previous predictions.[2,12] It should also be worth mentioning that the calculated total energy of model III is lower than the simple some of the total energies of one model I and two model II clusters by 4.7 eV at the B3LYP/6-31G(d) level. This substantial positive association energy clearly indicates that the sixfold coordinated silicon is energetically favored in the phosphate network. The stabilization presumably results from the delocalization of the negative charge on the nonbridging oxygens on P(Q^2) species through the conversion of P(Q^2) to P(Q^3) at the expense of the formation of the $^{[6]}$Si species. The present quantum-chemical calculations are hence in totally agreement with the proposed reaction scheme described in Eq. (3).

In model I, we assumed that the central $^{[4]}$Si unit was interconnected by four P[Q^3] units. It is interesting to note that even if we replace some of the P[Q^3] units in model I by P[Q^2] units, we obtained a similar association energy of ~4.6 eV as a result of the interaction with two model II-type clusters, resulting in a nearly regular octahedral Si configuration as shown in Fig. 4. We should also note that such a well-defined octahedral Si coordination was also obtained when two Na atoms in model III were replaced by one Ca atom. This implies that alkali earth cations can also behave as the charge compensator of the $[\mathrm{SiO}_{6/2}]^{2-}$ unit.

In conclusion, we have shown from MAS NMR and *ab initio* quantum-chemical studies on sodium phosphosilicate glasses that $^{[6]}$Si species are created through the interaction between two P[Q^2] units and one $^{[4]}$Si unit. The resulting octahedral unit shares only their "corners" with the adjacent phosphorous tetrahedral units; the additional nominal charges of the $^{[6]}$Si species are compensated by nearby alkali cations. The present structural model of $^{[6]}$Si may not be at variance with Zachariasen's rules for glass formation because the proposed structure does not force any periodicity on the glass network in spite of its overcoordinated state.

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訂正：4ページ目右列15段目記載の「in Fig.4」は「in Fig. 3 」の誤植です。

Erratum: Page 4, right column Line 14 “… shown in Fig. 4.” should be “… shown in Fig. 3.”