Structural Change around Si Atoms in P_2O_5–SiO_2 Binary Glasses before and after Annealing by ^{29}Si MAS NMR Spectroscopy

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The ^{29}Si MAS NMR spectra of P_2O_5–SiO_2 binary glasses were measured before and after annealing to examine the local structure around Si atoms in the glasses. The glasses were composed of SiO_6 octahedra and Q_4 (SiO_4 tetrahedra with four bridging oxygens). By increasing the P_2O_5 content, the fractions of SiO_6 octahedra increased and those of Q_4 decreased. The fractions of SiO_6 octahedra increased by 6–8% in the range of 29.7 to 47.4 mol % P_2O_5 by annealing for 5 h. This result was found for the first time in binary glasses. On the basis of the results obtained, the local structure around Si atoms in the glasses and the structural change by annealing are discussed.

P_2O_5-bearing silicate glasses are of considerable interest in material science such as glass-to-metal seals, laser hosts, optical fibers, bioglasses, and waste vitrification technology. Silicon atoms in most silicate glasses are tetrahedrally coordinated by four oxygen atoms. In phosphosilicate ternary glasses, however, the formation of SiO_6 octahedra has been reported by many studies.[1–7] The increase in the proportion of SiO_6 octahedra by a slower cooling rate has also been reported.[2,5,6] On the other hand, studies and information about the structure of phosphosilicate binary glasses[5–10] are much fewer than those of phosphosilicate ternary glasses.[1–7] Therefore, it is interesting to investigate the structures of phosphosilicate binary glasses and the structural change by annealing because annealing corresponds to a slower cooling rate.

In the present work, ^{29}Si MAS NMR spectra were measured for P_2O_5–SiO_2 binary glasses before and after annealing to reveal the local structure around Si atoms in the glasses and the structural change by annealing.

Phosphosilicate binary glasses with an $xP_2O_5\cdot(100-x)SiO_2$ composition ($x = 20$, 30, 40, 50, and 60) in mol % were prepared. 0.2 mol % Fe_2O_3 was added in order to shorten the relaxation time of the Si nucleus with $I = 1/2$. High-purity reagents of $NH_4H_2PO_4$, SiO_2, and Fe_2O_3 were used as starting materials. A 15–20 g batch of well-mixed reagents was calcined at 500 °C for 1 h and then melted at 1500 °C for 1 h in an alumina crucible covered with a lid. The melt was cooled to room temperature by removing the crucible from the furnace and placing the crucible directly onto a firebrick. Half of all the prepared glasses was annealed at the respective glass-transition temperatures for 5 h. All the prepared glasses before and after annealing were transparent and showed no sign of crystallization by XRD and phase separation by scanning electron microscopy (SEM; JEOL JSM-6300).

The compositions of the glasses were analyzed by chemical analysis. An amount of alumina contamination in the glasses was estimated by ^{27}Al MAS NMR. The glass transition temperatures (T_g) of the glasses were determined with a Rigaku Thermoflex TAS 300 TG 8110D TG-DTA. The measurements were carried out at a heating rate of $10\,K\cdot min^{-1}$. The ^{29}Si and ^{27}Al MAS NMR spectra of powdered P_2O_5–SiO_2 glasses were obtained at 59.584 and 78.160 MHz, respectively, with a Varian UNITY INOVA 300 MAS FT-NMR spectrometer (7.05 T). The acquisition parameters for ^{29}Si MAS NMR had a pulse length of 2.0 µs ($\pi/4$ pulse length), an accumulation of 10,000 scans and a pulse delay of 1.0 s. The spinning rate was 8.0 kHz. Polydimethylsilane was used as a secondary standard whose chemical shift was $\delta = -34.0$ ppm from TMS. The acquisition parameters for ^{27}Al MAS NMR had a pulse length of 0.6 µs ($\pi/18$ pulse length), an accumulation of 1000 scans and a pulse delay of 1.0 s. The spinning rate was 6.5 kHz. Chemical shifts were referenced to a 1 M $AlCl_3$ aqueous solution at 0 ppm.

The nominal and analyzed compositions, and T_g of the prepared glasses are given in Table 1. The actual compositions of the glasses deviated from the batch values because of evaporation of P_2O_5. Hereafter, the compositions of the glasses are described by analyzed compositions. The T_g of the glasses monotonously increased with an increase of P_2O_5 content. Alumina contamination in the glasses was within 1 mol % Al_2O_3.

Figures 1 and 2 show the ^{29}Si MAS NMR spectra of $xP_2O_5\cdot(100-x)SiO_2$ glasses ($x = 20.0$, 29.7, 36.5, 41.5, and 47.4) with no annealing and 5 h after annealing, respectively. The numerals in the figures denote isotropic chemical shifts (δ_{iso}). The spectra consist of one or two peaks. The large peaks with δ_{iso} values of -121 to -115 ppm and the small peaks of -217 to -213 ppm can be assigned to Q_4 (SiO_4 tetrahedra with four bridging oxygens) and SiO_6 octahedra,[11] respectively. Therefore, the formation of SiO_6 octahedra was observed from about 30 mol % P_2O_5.

The fractions of Q_4 and SiO_6 octahedra were estimated from the areas of the respective peaks. The error in the fractions of Q_4 and SiO_6 octahedra was within ±1%. The fractions of Q_4 (top) and SiO_6 octahedra (bottom) as functions of the P_2O_5 content in

Table 1. Nominal and analyzed compositions and glass-transition temperatures (T_g) of P_2O_5–SiO_2 glasses

Glass composition/mol %		T_g/°C
Nominal	Analyzed	
$20P_2O_5\cdot80SiO_2$	$20.0P_2O_5\cdot80.0SiO_2$	523
$30P_2O_5\cdot70SiO_2$	$29.7P_2O_5\cdot70.3SiO_2$	536
$40P_2O_5\cdot60SiO_2$	$36.5P_2O_5\cdot63.5SiO_2$	545
$50P_2O_5\cdot50SiO_2$	$41.5P_2O_5\cdot58.5SiO_2$	550
$60P_2O_5\cdot40SiO_2$	$47.4P_2O_5\cdot52.6SiO_2$	562

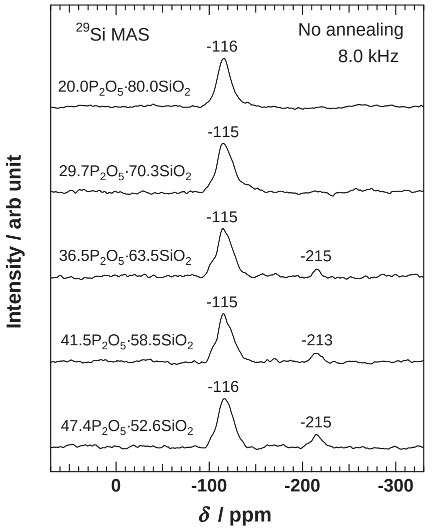

Figure 1. ^{29}Si MAS NMR spectra of xP$_2$O$_5$•$(100 - x)$SiO$_2$ glasses ($x = 20.0$, 29.7, 36.5, 41.5, and 47.4) with no annealing.

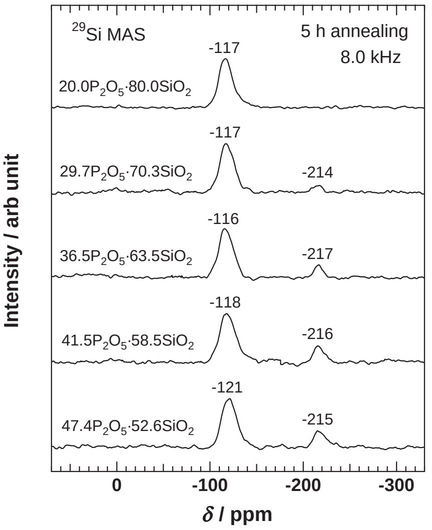

Figure 2. ^{29}Si MAS NMR spectra of xP$_2$O$_5$•$(100 - x)$SiO$_2$ glasses ($x = 20.0$, 29.7, 36.5, 41.5, and 47.4) after 5 h annealing.

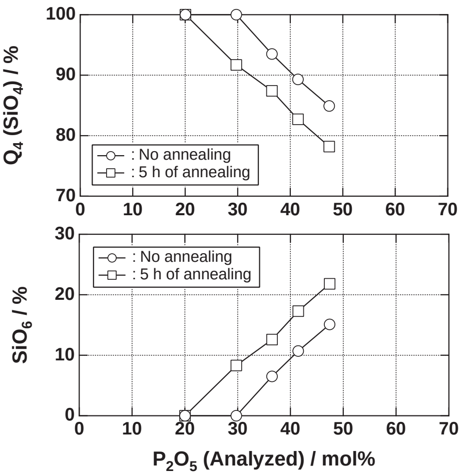

Figure 3. Plots of the fractions of Q$_4$ (top) and SiO$_6$ octahedra (bottom) as functions of P$_2$O$_5$ content in P$_2$O$_5$–SiO$_2$ glasses.

P$_2$O$_5$–SiO$_2$ glasses are plotted in Figure 3. The fraction of SiO$_6$ octahedra in the glasses containing 20.0 mol % P$_2$O$_5$ and 29.7P$_2$O$_5$•70.3SiO$_2$ glass with no annealing is 0%. By increasing the P$_2$O$_5$ content, the fractions of SiO$_6$ octahedra increase and those of Q$_4$ decrease almost linearly from 20 and 29.7 mol % P$_2$O$_5$ in glasses with 5 h annealing and no annealing, respectively. Thus, the increase of the P$_2$O$_5$ content is considered to make the formation of SiO$_6$ octahedra easy. The fractions of SiO$_6$ octahedra increase by 6–8% in the range of 29.7 to 47.4 mol % P$_2$O$_5$ by 5 h annealing, indicating that the formation of SiO$_6$ octahedra by annealing makes the glasses more thermodynamically stable. By the way, crystalline SiP$_2$O$_7$ consists of SiO$_6$ octahedra and PO$_4$ tetrahedra.[12] Therefore, the formation of SiO$_6$ octahedra in the glasses is considered to be caused by the formation of a more thermodynamically stable local structure, as seen in crystalline SiP$_2$O$_7$. The maximum fraction of SiO$_6$ octahedra in this work is 21.8% and smaller than the fractions of SiO$_6$ octahedra observed in phosphosilicate ternary glasses.[1–4] This suggests that the formation of SiO$_6$ octahedra is mainly due to the charge compensation by the third oxide (except P$_2$O$_5$ and SiO$_2$) but also somewhat due to the formation of a more thermodynamically stable local structure, as seen in crystalline SiP$_2$O$_7$.

In conclusion, P$_2$O$_5$–SiO$_2$ binary glasses are composed of SiO$_6$ octahedra and Q$_4$. The formation of SiO$_6$ octahedra is observed from about 30 mol % P$_2$O$_5$. By increasing the P$_2$O$_5$ content, the fractions of SiO$_6$ octahedra increase and those of Q$_4$ decrease almost linearly from 20 and 29.7 mol % P$_2$O$_5$ in the glasses with 5 h annealing and no annealing, respectively. The fractions of SiO$_6$ octahedra increase by 6–8% in the range of 29.7 to 47.4 mol % P$_2$O$_5$ by 5 h annealing. The formation of SiO$_6$ octahedra in the glasses is considered to be caused by the formation of a more thermodynamically stable local structure, as seen in crystalline SiP$_2$O$_7$.

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