

Structural Change around Si Atoms in P₂O₅-SiO₂ Binary Glasses before and after Annealing by ²⁹Si MAS NMR Spectroscopy

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The ²⁹Si MAS NMR spectra of P₂O₅-SiO₂ binary glasses were measured before and after annealing to examine the local structure around Si atoms in the glasses. The glasses were composed of SiO₆ octahedra and Q₄ (SiO₄ tetrahedra with four bridging oxygens). By increasing the P₂O₅ content, the fractions of SiO₆ octahedra increased and those of Q₄ decreased. The fractions of SiO₆ octahedra increased by 6–8% in the range of 29.7 to 47.4 mol % P₂O₅ 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.

P₂O₅-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 SiO₆ octahedra has been reported by many studies.^{1–7} The increase in the proportion of SiO₆ 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, ²⁹Si MAS NMR spectra were measured for P₂O₅-SiO₂ 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 xP₂O₅·(100-x)-SiO₂ composition (x = 20, 30, 40, 50, and 60) in mol % were prepared. 0.2 mol % Fe₂O₃ was added in order to shorten the relaxation time of the Si nucleus with I = 1/2. High-purity reagents of NH₄H₂PO₄, SiO₂, and Fe₂O₃ 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 ²⁷Al 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·min⁻¹. The ²⁹Si and ²⁷Al MAS NMR spectra of powdered P₂O₅-SiO₂ 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 ²⁹Si MAS NMR had a pulse length of 2.0 μs (π/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 δ = -34.0 ppm from TMS. The acquisition parameters for ²⁷Al MAS NMR had a pulse length of 0.6 μs (π/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 AlCl₃ 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 P₂O₅. Hereafter, the compositions of the glasses are described by analyzed compositions. The *T_g* of the glasses monotonously increased with an increase of P₂O₅ content. Alumina contamination in the glasses was within 1 mol % Al₂O₃.

Figures 1 and 2 show the ²⁹Si MAS NMR spectra of xP₂O₅·(100-x)SiO₂ 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 Q₄ (SiO₄ tetrahedra with four bridging oxygens) and SiO₆ octahedra,¹¹ respectively. Therefore, the formation of SiO₆ octahedra was observed from about 30 mol % P₂O₅.

The fractions of Q₄ and SiO₆ octahedra were estimated from the areas of the respective peaks. The error in the fractions of Q₄ and SiO₆ octahedra was within ±1%. The fractions of Q₄ (top) and SiO₆ octahedra (bottom) as functions of the P₂O₅ content in

Table 1. Nominal and analyzed compositions and glass-transition temperatures (*T_g*) of P₂O₅-SiO₂ glasses

Glass composition/mol %		<i>T_g</i> /°C
Nominal	Analyzed	
20P ₂ O ₅ ·80SiO ₂	20.0P ₂ O ₅ ·80.0SiO ₂	523
30P ₂ O ₅ ·70SiO ₂	29.7P ₂ O ₅ ·70.3SiO ₂	536
40P ₂ O ₅ ·60SiO ₂	36.5P ₂ O ₅ ·63.5SiO ₂	545
50P ₂ O ₅ ·50SiO ₂	41.5P ₂ O ₅ ·58.5SiO ₂	550
60P ₂ O ₅ ·40SiO ₂	47.4P ₂ O ₅ ·52.6SiO ₂	562

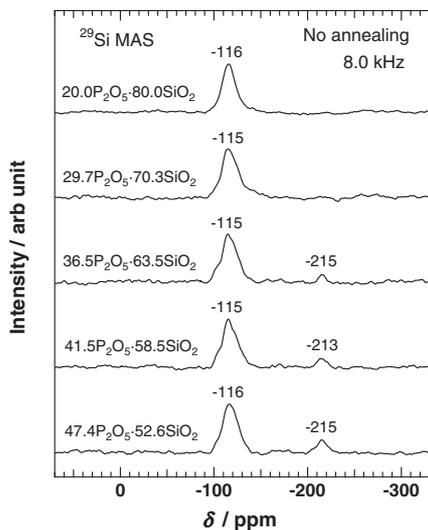


Figure 1. ^{29}Si MAS NMR spectra of $x\text{P}_2\text{O}_5 \cdot (100 - x)\text{SiO}_2$ glasses ($x = 20.0, 29.7, 36.5, 41.5,$ and 47.4) with no annealing.

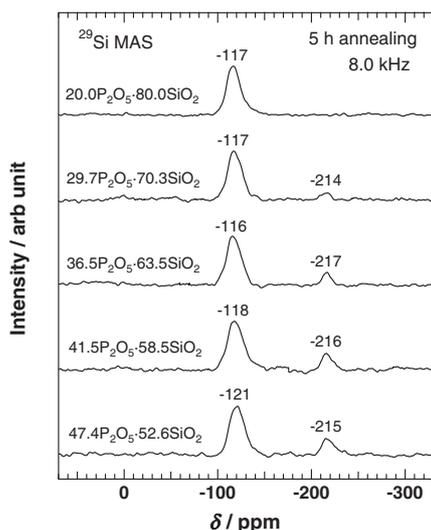


Figure 2. ^{29}Si MAS NMR spectra of $x\text{P}_2\text{O}_5 \cdot (100 - x)\text{SiO}_2$ glasses ($x = 20.0, 29.7, 36.5, 41.5,$ and 47.4) after 5 h annealing.

P_2O_5 - SiO_2 glasses are plotted in Figure 3. The fraction of SiO_6 octahedra in the glasses containing 20.0 mol % P_2O_5 and $29.7\text{P}_2\text{O}_5 \cdot 70.3\text{SiO}_2$ glass with no annealing is 0%. By increasing the P_2O_5 content, the fractions of SiO_6 octahedra increase and those of Q_4 decrease almost linearly from 20 and 29.7 mol % P_2O_5 in glasses with 5 h annealing and no annealing, respectively. Thus, the increase of the P_2O_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_2O_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_2O_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_2O_7 . The maximum fraction of SiO_6 octahedra in this work is 21.8% and smaller than

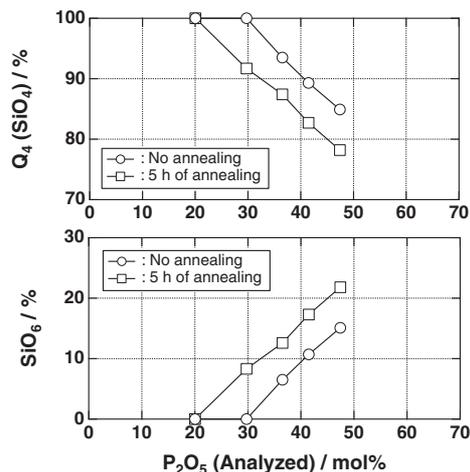


Figure 3. Plots of the fractions of Q_4 (top) and SiO_6 octahedra (bottom) as functions of P_2O_5 content in P_2O_5 - SiO_2 glasses.

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_2O_5 and SiO_2) but also somewhat due to the formation of a more thermodynamically stable local structure, as seen in crystalline SiP_2O_7 .

In conclusion, P_2O_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_2O_5 . By increasing the P_2O_5 content, the fractions of SiO_6 octahedra increase and those of Q_4 decrease almost linearly from 20 and 29.7 mol % P_2O_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_2O_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_2O_7 .

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