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# Simulation for elucidating the formation mechanism of 6-coordinated Si in phosphate glass

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## Abstract

Six-coordinated Si ($^{[6]}$Si) structures are readily formed in silicophosphate glasses with high $P_2O_5$ contents. Although experiments and simulations have provided some information on the local configurations around $^{[6]}$Si, further research on the formation mechanism of $^{[6]}$Si at the atomic scale is needed. To investigate the formation mechanism of $^{[6]}$Si, we performed dynamic and static analyses based on first-principles calculations. We observed that the coordination number of Si increased, and the P-$Q^2$ (P-$Q^n$, where $n$ represents the number of bridging oxygen atoms) changed to P-$Q^3$. Atomic energy analysis revealed that the energy decreases with the structural change from P-$Q^2$ to P-$Q^3$ exceeded the energy increase with an increase in the coordination number of Si, stabilizing of the entire system.

## 1. Introduction

There is an increasing demand for biomaterials that can stimulate osteoblasts by incorporating inorganic ions such as $Ca^{2+}$ and $Mg^{2+}$ into bone. Water-soluble phosphate glasses can promote bone regeneration by releasing inorganic ions as bone-formation-promoting factors, and the dissolution of these ions from the glass must be reasonably controlled. Our group has focused on proton conduction, which is the trigger of ion solubility, and reported that ion behavior differs depending on the network morphology of $PO_4$ tetrahedra (P-: number of bridging oxygen) in the glass, where protons can diffuse much more easily near P-$Q^2$ than near P-$Q^3$. [1] Thus, the dispersion of P-$Q^3$ throughout the glass is anticipated to suppress proton conduction and, as a result, the control of solubility. Furthermore, we found that six-coordinated Si ($^{[6]}$Si) preferentially coordinated with P-$Q^3$. [2] It can be believed that the formation of nanostructured $^{[6]}$Si enables the control of solubility, but the formation mechanism of $^{[6]}$Si is not clear. In this study, we aim to elucidate the formation mechanism of $^{[6]}$Si in phosphate glasses based on first-principles molecular dynamics (MD) simulations.

## 2. Computational method

We considered a glass model with an experimentally obtained composition ratio of $55.0P_2O_5$-$21.3SiO_2$-$23.7Na_2O$ (mol%). First, we generated a model in which all Si atoms were four-coordinated through CL-MD simulations with adjusted empirical parameters with the DL_POLY code. [3] Subsequently, first-principles MD simulations using the SIESTA code [4] were performed to observe the reaction process from $^{[4]}$Si to $^{[5/6]}$Si. Atomic energies were calculated using orbital decomposition of the total energy by the OpenMX code. [5] For these electronic structure calculations, a localized basis with the GGA-PBE functional was used.

## 3. Results and discussion

We observed the following behavior, as shown in Figs. 1(a) and 1(b). The nonbridging oxygen (NBO) —indicated by an arrow— formed a bond with neighboring Si. The NBO coordinated with P-$Q^2$ coordinates with the neighboring $^{[4]}$Si, forming P-$Q^3$ and $^{[5]}$Si. Na coordinated with the NBO dissociates from this O. This reaction is consistent with predictions from the experimental results. We also found that Na plays a role in compensating for the charge of NBO. We analyzed the atomic energies to investigate the cause of the structural change from lower-energy $^{[4]}$Si to higher-energy $^{[5]}$Si as shown in Fig. 2. The energy around Si increased, whereas that around P decreased. Therefore, the region around Si becomes unstable owing to the increase in the coordination number of Si. However, the simultaneous structural change from P-$Q^2$ to P-$Q^3$ stabilizes the entire system.

## 4. Conclusions

We focused on the unique $^{[6]}$Si structure that appears in silicophosphate glass. To investigate the formation mechanism of $^{[6]}$Si, we performed dynamic and static analyses based on first-principles calculations. Using FP-MD simulations, we observed the reaction " $^{[4]}$Si + P-$Q^2$ → $^{[5]}$Si + P-$Q^3$ ". Through atomic energy analysis, we found that the energy decrease with an increase in P-$Q^n$ exceeds the energy increase with an increase in the coordination number of Si, stabilizing the entire system. We conclude that the key factor in the formation of $^{[6]}$Si is the energy decrease associated with the change from the NBO in the $PO_4$ tetrahedron to BO.

## References

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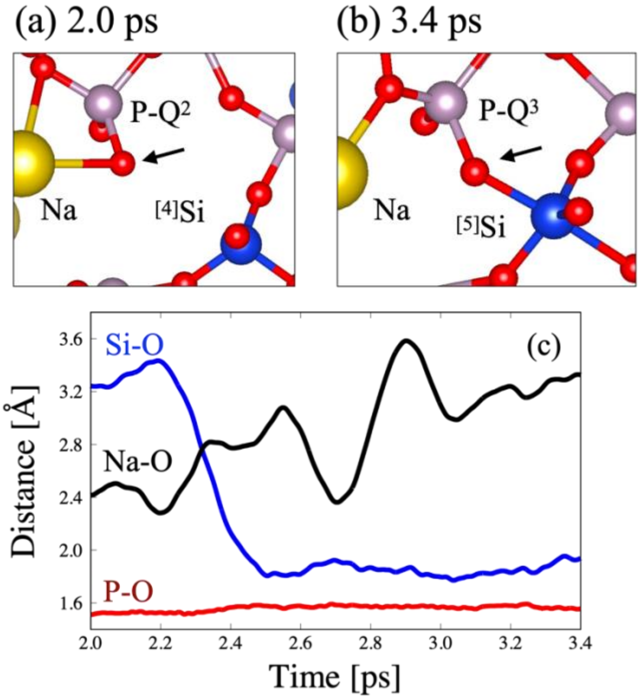

Fig.1 Snapshots of chemical reactions near P-$Q^2$ at (a) 2.0 and (b) 3.4 ps. (c) Time evolution of interatomic distances related to the formation of a new bond.

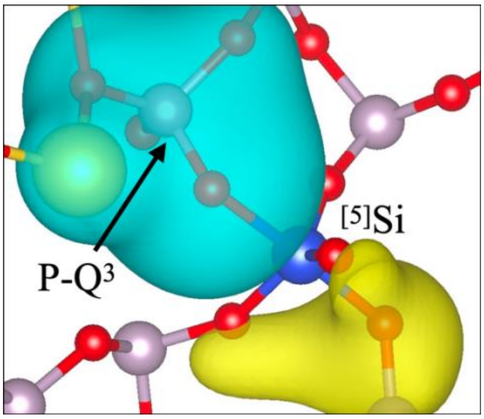

Fig.2 Distribution of energy regions within the glass model. Regions of increased energy are shown in yellow, and regions of decreased energy are shown in blue.