Different structural behavior of MgSiO₃ and CaSiO₃ glasses at high pressures

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Abstract

Knowledge of the structural behavior of silicate melts and/or glasses at high pressures provides fundamental information for discussing the nature and properties of silicate magmas in the Earth's interior. The behavior of Si-O structures under high-pressure conditions has been widely studied, while the effect of cation atoms on the high-pressure structural behavior of silicate melts or glasses has not been well investigated. In this study, we investigated the structures of MgSiO₃ and CaSiO₃ glasses up to 5.4 GPa by in situ X-ray pair distribution function measurements to understand the effect of different cations (Mg²⁺ and Ca²⁺) on high-pressure structural behavior of silicate glasses. We found that the structural behavior of MgSiO₃ and CaSiO₃ glasses are different at high pressures. The structure of MgSiO₃ glass changes by shrinking of Si-O-Si angle with increasing pressures, which is consistent with previous studies for SiO₂ and MgSiO₃ glasses. On the other hand, CaSiO₃ glass shows almost no change in Si-Si distance at high pressures, while the intensities of two peaks at \sim 3.0 and \sim 3.5 Å change with increasing pressure. The structural change in CaSiO₃ glass at high pressure is interpreted as the change in the fraction of the edge-shared and corner-shared CaO_6 -SiO₄ structures. The different high-pressure structural behavior observed in MgSiO₃ and CaSiO₃ glasses may be the origin of differences in properties, such as viscosity between MgSiO₃ and CaSiO₃ melts at high pressures. This signifies the importance of different structural behaviors due to different cations in investigations of the nature and properties of silicate magmas in Earth's interior.

Keywords: Glass structure, MgSiO₃, CaSiO₃, pair distribution function, high pressure

INTRODUCTION

Structures of silicate melts strongly influence physical properties such as density, viscosity, and diffusivity (e.g., Sakamaki et al. 2013; Sanloup et al. 2013; Wang et al. 2014; Bajgain et al. 2015), and therefore knowledge of the structural behavior of silicate melts and/or glasses under high-pressure conditions is fundamental in understanding the nature and properties of silicate magmas in the Earth's interior. Since structural investigation of silicate melts under in situ high-pressure and high-temperature conditions is still challenging due to technical difficulties, silicate glasses have been studied at high pressures under room-temperature conditions as an analog of silicate melts. Pressure-induced structural changes of SiO₂ glass have been the most studied as the simplest silicate composition by using in situ high-pressure techniques (e.g., Sato and Funamori 2008; Benmore et al. 2010; Murakami and Bass 2010; Prescher et al. 2017; Lee et al. 2019; Petitgirard et al. 2019; Kono et al. 2020; Andrault et al. 2020; Kono et al. 2022), which provide important knowledge on the behavior of the Si-O structure under high-pressure conditions.

In addition, MgSiO₃ glass also has been studied by several researchers as a representative composition of silicate magma in the Earth's interior (e.g., Lee et al. 2008; Kono et al. 2018; Salmon et al. 2019; Ryu et al. 2022). However, the structural behavior of other silicate glasses with different compositions remains poorly investigated at in situ high-pressure conditions.

In this study, we investigate the structures of MgSiO₃ and CaSiO₃ glasses at high-pressure conditions, up to 5.4 GPa, using in situ pair distribution function measurements to understand the effect of different cations (Mg2+ and Ca2+) on the highpressure structural behavior of silicate glasses. MgSiO₃ and CaSiO₃ glasses are the end-member pyroxene compositions, and therefore knowledge of the structural behavior of MgSiO₃ and CaSiO₃ glasses at high pressures would provide important clues to understanding the structure and properties of silicate magmas in the Earth's upper mantle. At ambient pressure conditions, structures of MgSiO₃ and CaSiO₃ glasses have been studied by neutron diffraction (e.g., Cormier and Cuello 2011), high-energy X-ray diffraction (Kohara et al. 2011), Raman spectroscopy (e.g., Kalampounias et al. 2009), and nuclear magnetic resonance (NMR) spectroscopy (e.g., Kaseman et al. 2015). On the other hand, structural investigations of these glasses at in situ

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high-pressure conditions are still limited, although there are several structural analyses at ambient pressure of silicate glasses synthesized at high-pressure conditions (Shimoda et al. 2005). Nevertheless, the structure of MgSiO₃ glass at in situ high-pressure conditions has been studied by some previous studies using neutron diffraction (Salmon et al. 2019), X-ray diffraction (Kono et al. 2018; Ryu et al. 2022), and X-ray Raman scattering (Lee et al. 2008) measurements. In contrast, the structure of CaSiO₃ glass has not been well studied at in situ high-pressure conditions. To the best of our knowledge, only Kubicki et al. (1992) and Salmon et al. (2019) investigated the structure of CaSiO₃ glass at in situ high-pressure conditions. Kubicki et al. (1992) conducted in situ Raman spectroscopy and infrared absorption measurements on CaSiO₃ glasses in a DAC (diamond-anvil cell) at 11-35 GPa. Salmon et al. (2019) investigated the structure of CaSiO₃ and MgSiO₃ glasses from ambient pressure to 17.5 GPa by using in situ neutron diffraction measurement and molecular dynamics (MD) simulations. Salmon et al. (2019) showed that the M-O (M = Mg, Ca) coordination number of both $CaSiO_3$ and MgSiO₃ glasses increases at high pressures in a similar manner. The nearest neighbor Si-O and M-O distances show slight increase with increasing pressure from ambient pressure to 17.5 GPa (1.61 to 1.62 Å for Si-O distance of MgSiO₃ glass; 1.62 to 1.63 Å for Si-O distance of CaSiO₃ glass; 1.99–2.02 Å for Mg-O distance in MgSiO₃ glass; 2.32–2.35 Å for Ca-O distance in CaSiO₃ glass). Mg-O coordination number in MgSiO₃ glass changes from 4.50 at ambient pressure to 6.20 at 17.5 GPa, and Ca-O coordination number in CaSiO₃ glass changes from 6.15 at ambient pressure to 7.41 at 17.5 GPa. These data indicate that the nearest neighbor structures in MgSiO3 and CaSiO3 glasses change similarly with increasing pressure. However, the study of Salmon et al. (2019) was limited only to the nearest neighbor Si-O and M-O distances due to weak scattering of Si and Ca in neutron diffraction measurements, and intermediate range structures such as Si-Si, Ca-Si, and Ca-Ca distances were not investigated in Salmon et al. (2019).

In this study, we investigated structures of MgSiO₃ and CaSiO₃ glasses at high pressures up to 5.4 GPa, by using in situ X-ray diffraction measurements to understand the effect of different cations (Mg and Ca) on the high-pressure structural behavior, not only for the nearest Si-O and M-O distances but also for the intermediate Si-Si, M-Si, and M-M distances. We found different behaviors in the intermediate range structures of MgSiO₃ and CaSiO₃ glasses at high-pressure conditions.

EXPERIMENTAL METHODS

CaSiO₃ and MgSiO₃ samples were prepared by mixing powders of SiO₂, CaCO₃, and/or MgO. Powders of these oxides and carbonates were dried at 110 °C for >24 h before weighing and were mixed in an agate mortar with ethanol for 1–2 h. Glass samples were prepared in an aerodynamic levitation furnace with CO₂ laser heating at ~1800–2100 °C at the Geodynamics Research Center (GRC), Ehime University. Chemical compositions of the synthesized glass samples were confirmed by using JEOL JM-7000F field-emission scanning electron microscope (FE-SEM) with energy-dispersive spectroscopy (EDS) at GRC (Online Materials¹ Table S1). Densities of the CaSiO₃ (2.80 ± 0.05 g/cm³) and MgSiO₃ (2.68 ± 0.06 g/cm³) glasses were measured by Archimedes' method.

High-energy X-ray diffraction measurements of the CaSiO₃ and MgSiO₃ glasses at ambient pressure were conducted at the BL04B2 beamline of the SPring-8. The dedicated X-ray diffractometer with six-point detectors (four cadmium telluride detectors and two germanium detectors) at the BL04B2 beamline enables us to conduct accurate pair distribution function (PDF) analysis with high real-space resolution (Ohara et al. 2020). We used spherical glass samples of 1.8 mm diameter, which were placed in a vacuum chamber under room-temperature conditions. High-energy X-ray diffraction measurements using monochromatic X-rays of 61.4 keV were carried out by scanning the 20 angle from 0.3 to 49°, which covers the range of the momentum transfer Q up to 25.5 Å⁻¹. The X-ray diffraction data were analyzed by using the standard analysis procedures of the BL04B2 beamline (Kohara et al. 2007).

High-pressure experiments for CaSiO₃ and MgSiO₃ glasses were carried out by using a Paris-Edinburgh (PE) press with a standard PE cell assembly of the 16-BM-B beamline in the Advanced Photon Source (APS) (Kono et al. 2014). Cup-shaped WC anvils with the cup diameter of 12 mm and a bottom diameter of 3 mm were used. The cell assembly mainly consists of BN capsule surrounded by an inner MgO ring and outer boron-epoxy (BE) gaskets with ZrO₂ caps at the top and bottom of the cell. Pressure was determined by X-ray diffraction measurement of the MgO ring, with the equation of state of MgO (Kono et al. 2010), for the CaSiO₃ glass experiment, and of Au foil, which is inserted between the MgO ring and BN capsule, using the equation of state of Tsuchiya (2003), for the MgSiO₃ glass experiment. Densities of CaSiO₃ and MgSiO₃ glasses at high-pressure conditions are calculated based on the densities of CaSiO₃ ($2.80 \pm 0.05 g/cm^3$) and MgSiO₃ ($2.68 \pm 0.06 g/cm^3$) glasses measured at ambient pressure by Archimedes' method and the pressure-volume relation of CaSiO₃ and MgSiO₃ glasses reported in Salmon et al. (2019).

Pair distribution function measurement of CaSiO₃ glass at high pressures was carried out by a multi-angle energy-dispersive X-ray diffraction technique combined with the PE cell at the 16-BM-B beamline of the APS. A large Huber stage holding a germanium solid-state detector allows precise control of 2θ angles, and energydispersive X-ray diffraction measurements using fine collimation slits enable us to collect clean signals from glass samples without background noise from the surrounding pressure medium materials (Kono et al. 2014). We collected energy-dispersive X-ray diffraction patterns at the 2θ angles of 3, 4, 5, 7, 9, 12, 16, 22, 28, and 35°. The energy-dispersive X-ray diffraction spectra were analyzed by using an analysis program developed by Changyong Park and Rostislav Hrubiak at the 16-BM-B beamline (Kono et al. 2014). We obtained the S(Q) of CaSiO₃ glass at the Q range up to 17.0 Å⁻¹ under the pressure conditions from 0.8 to 5.4 GPa at room temperature.

Pair distribution function measurement of MgSiO3 glass at high pressures was conducted at the BL37XU beamline of the SPring-8. We used a monochromatic X-ray of 37.4 keV. The X-ray was focused from 1.0 to 0.2 mm horizontal with 0.7 m long horizontal-deflection mirrors so as to increase an available flux. The structure of MgSiO3 glass was measured up to 5.2 GPa in the PE cell by high-energy X-ray diffraction measurement using a cadmium telluride point detector (Amptek X-123) with a double slit collimation setup in front of the detector. The double slit collimation setup yields collimation length of <1.8 mm at the sample position at 20 angles higher than ~9° to avoid background noise. The size of the incident slit and two collimation slits were adjusted with varying 20 angles to maximize the intensity of the signal by increasing collimation length within the diameter of MgSiO3 glass sample. High-energy X-ray diffraction measurements for MgSiO3 glass at high pressures were carried out by scanning the 20 angle from 1 to 60°. Analysis was conducted by using the method developed at the BL04B2 beamline of the SPring-8 (Ohara et al. 2020). We obtained the S(Q) of MgSiO3 glass at the Q range up to 15.0 Å-1 under the pressure conditions from 1.0 to 5.2 GPa at room temperature.

It is important to note that both experiments at BL37XU beamline at SPring-8 (MgSiO₃ glass experiment) and at 16-BM-B beamline at APS (CaSiO₃ glass experiment) used a collimation slit set up in front of the detector. The collimation slit setup enables us to collect the XRD signal only from the sample at the 20 angle higher than -9° for the MgSiO₃ glass experiment and at the 20 angle higher than -3° for the CaSiO₃ glass experiment. Since the collimation slit setup eliminates background noise not only from the high-pressure cell assemblies but also from different beamline components, we can obtain comparable data.

The pair distribution function g(r) was obtained by Fourier transmission of the Faber-Ziman total structure factor S(Q) (Faber and Ziman 1965). The Lorch function was applied to remove the truncation effect on the final pair distribution function determination (Lorch 1969). The positions of the peaks of the g(r) showing discernible separation were determined by using simple Gaussian peak fitting. On the other hand, Si-Si, Mg-Si, and Mg-Mg peaks in MgSiO₃ glass, and Ca-O and O-O peaks in CaSiO₃ glass overlap each other. For the overlapping peaks, we used a multi-peak fitting method described by de Grouchy et al. (2017). In the de Grouchy et al. (2017)'s method, the g(r) is the sum of all the individual ion-ion interactions within the sample, where each ion-ion contribution is represented by a Gaussian peak, $g(r)_{ind}$. The g(r) is fit using the following equations:

$$g(r) = \sum g(r)_{\text{ind}} = \frac{1}{n_0 S} \sum_i \frac{x_i A_i}{\sigma_{i\sqrt{2\pi}}} \exp\left(\frac{-(r-d_i)^2}{2\sigma_i^2}\right)$$
(1)

where

$$A_{i} = \frac{CN_{i}}{\int \frac{4\pi r^{2}}{\sigma_{i}\sqrt{2\pi}} \exp\left(\frac{\left(r-d_{i}\right)^{2}}{2\sigma_{i}^{2}}\right) dr}$$
(2)

where CN_i is coordination number for individual ion-ion contributions, n_0 is the number density, x_i is a concentration of the species, and d_i is interatomic distance. σ_i is calculated from $k\sqrt{d_i}$, which defines the width and height of the individual Gaussian peak. k is an adjustable parameter (Hosemann and Bagchi 1962), with values ranging from 0.06 to 0.15 depending on the ion-ion contribution.

RESULTS

Structure of MgSiO₃ and CaSiO₃ glasses at ambient pressure

Figures 1a and 1b show the S(Q) and g(r) of MgSiO₃ glass at ambient pressure, respectively. The g(r) of MgSiO₃ glass shows peaks at $r_1 = 1.621 \pm 0.002$ Å, $r_2 = 2.030 \pm 0.004$ Å, $r_3 = 2.618 \pm$ 0.009 Å, and $r_4 = 3.179 \pm 0.006$ Å. A first-principles molecular dynamics simulation of MgSiO₃ glass reports bond distances of Si-O = 1.63 Å, Mg-O = 1.98 Å, O-O = 2.68 Å, Si-Si = 3.02 Å, Mg-Si =3.22 Å, and Mg-Mg = 3.42 Å (Ghosh et al. 2014), indicating that the r_1 , r_2 , and r_3 peaks obtained in this study correspond to Si-O, Mg-O, and O-O distances, respectively. The r_4 peak is considered as the overlapping of Si-Si, Mg-Si, and Mg-Mg distances. The S(Q) and g(r) of CaSiO₃ glass at ambient pressure are shown in Figures 1c and 1d, respectively. The g(r) of CaSiO₃ glass shows the peak positions at $r_1 = 1.622 \pm 0.001$ Å, $r_2 = 2.335 \pm 0.008$ Å, $r_3 = 2.623 \pm 0.012$ Å, $r_4 = 3.017 \pm 0.008$ Å, and $r_5 = 3.573 \pm 0.014$ Å, which are considered as Si-O, Ca-O, O-O, overlapping Si-Si/Ca-Si, and overlapping Ca-Si/Ca-Ca distances, respectively (Cormier and Cuello 2013; Mead and Mountjoy 2006a, 2006b). According to a molecular dynamics simulation study (Mead and Mountjoy 2006a, 2006b), Si-Si and Ca-Si distances overlap at the same distance at around 3.1 Å, and Ca-Si and Ca-Ca distances also overlap at around 3.6 Å.

Structures of MgSiO₃ and CaSiO₃ glasses at high pressures

Figures 2a and 2b show the S(Q) and g(r) of MgSiO₃ glass from 1.0 to 5.2 GPa. With increasing pressure, the intensity of the first sharp diffraction peak (FSDP) of MgSiO₃ glass decreases, and the FSDP position shifts toward high Q (Figs. 2a and 3). The highpressure behavior of the FSDP is consistent with those reported in previous MgSiO₃ glass studies (e.g., Ryu et al. 2022). On the other hand, the S(Q) of MgSiO₃ glass shows negligible change at $Q > 3 Å^{-1}$ at high-pressure conditions up to 5.2 GPa. The g(r) of MgSiO₃ glass shows clear r_1 (Si-O) and r_4 (Si-Si/Mg-Si/Mg-Mg) peaks (Fig. 2b). On the other hand, the r_2 (Mg-O) peak is identified as a shoulder peak on the high r side of the r_1 (Si-O) peak,



FIGURE 1. Structure factor, S(Q), and pair distribution function, g(r), of MgSiO₃ glass (**a** and **b**) and of CaSiO₃ glass (**c** and **d**) at ambient pressure. (**b**) r_1 , r_2 , r_3 , and r_4 are Si-O, Mg-O, O-O, and Si-Si/Mg-Mg distances, respectively. (**d**) r_1 , r_2 , r_3 , r_4 and r_5 are Si-O, Ca-O, O-O, Si-Si, and Ca-Si/Ca-Ca distances, respectively. (Color online.)



FIGURE 2. Structure factor, S(Q), and pair distribution function, g(r), of MgSiO₃ glass (**a** and **b**) and CaSiO₃ glass (**c** and **d**) at high pressures. (**b**) r_1 , r_2 , and r_4 are Si-O, Mg-O, and Si-Si/Mg-Si/Mg-Mg distances, respectively. (**d**) r_1 , r_2 , r_4 and r_5 are Si-O, Ca-O, Si-Si, and Ca-Si/Ca-Ca distances, respectively. (**c**lor online.)

and the r_3 (O-O) peak is not visible. This is due to the broadening of the peak width of g(r) by a narrower range of Q (15 Å⁻¹) in the S(Q) data obtained in the high-pressure experiments. Online Materials¹ Figure S1 shows the effect of the maximum $Q(Q_{max})$ range on the g(r) simulated by using the ambient pressure data. The resolution of the g(r) is defined as $2\pi/Q_{\text{max}}$ (e.g., Lorch 1969), and the peak width of g(r) becomes broader by reducing the Q_{max} . In Online Materials¹ Figure S1a, the g(r) result simulated with the $Q_{\text{max}} = 15 \text{ Å}^{-1}$ shows the r_2 peak as the shoulder peak of the r1 peak, similarly to the high-pressure experimental result, and it is difficult to identify the r₃ peak. On the other hand, the peak positions of g(r) determined from the result of $Q_{\text{max}} = 15 \text{ Å}^{-1}$ (r₁ = 1.619 ± 0.003 Å; $r_2 = 2.029 \pm 0.010$ Å; $r_4 = 3.183 \pm 0.003$ Å; r_3 is fixed at 2.618 Å) are comparable to those obtained from the data of $Q_{\text{max}} = 25 \text{ Å}^{-1} (r_1 = 1.621 \pm 0.002 \text{ Å}; r_2 = 2.030 \pm 0.004 \text{ Å};$ $r_3 = 2.618 \pm 0.003$ Å; $r_4 = 3.179 \pm 0.003$ Å). Therefore, the peak positions of the g(r) of MgSiO₃ glass at high pressures determined from the S(Q) of $Q_{\text{max}} = 15 \text{ Å}^{-1}$ are considered to be comparable to those determined at ambient pressure. The g(r) of MgSiO₃ glass at high pressures shows almost no change in the r1 and r2 peaks up to 5.2 GPa, while the position of the r₄ peak decreases with increasing pressure (Fig. 2b).

Figures 2c and 2d show the S(Q) and g(r) of CaSiO₃ glass from 0.8 to 5.4 GPa. In contrast to the marked change in the FSDP of MgSiO₃ glass at high pressures, the S(Q) of CaSiO₃ glass shows only small changes in the intensity and position of the FSDP at high pressures (Figs. 2c and 3). On the other hand, the second and third peak features in the S(Q) at around 4–6 Å⁻¹ shift toward high Q with increasing pressure (Fig. 2c). The g(r)of CaSiO3 glass obtained at high pressures show clear r1 (Si-O), r₂ (Ca-O), r₄ (Si-Si/Ca-Si), and r₅ (Ca-Si/Ca-Ca) peaks (Fig. 2d). The Ca-O peak of the g(r) in CaSiO₃ glass can be well identified even at the narrower range of Q_{max} (17 Å⁻¹) in the S(Q) of the high-pressure experiments (Online Materials¹ Fig. S1a), because of the longer distance of the Ca-O peak in CaSiO3 glass compared to the Mg-O peak in MgSiO3 glass. In addition, comparison of the peak positions of CaSiO₃ glass at ambient pressure determined by a Q range of 17 Å⁻¹ ($r_1 = 1.614 \pm 0.003$ Å; $r_2 = 2.358 \pm 0.008$ Å; r_4 = 3.077 \pm 0.165 Å; r_5 = 3.560 \pm 0.021 Å) and of 25 Å^{-1} (r_1 = 1.622 ± 0.001 Å; $r_2 = 2.335 \pm 0.008$ Å; $r_4 = 3.017 \pm 0.008$ Å; $r_5 =$ 3.573 ± 0.014 Å) show similar values. The r₁ and r₂ peaks of the g(r) of CaSiO₃ glass stay almost the same up to 5.4 GPa, whereas there are marked changes in the intensity of the r₄ and r₅ peaks with increasing pressure (Fig. 2d). The intensity of the r₄ peak

markedly increases with increasing pressure, accompanied by the decrease of the intensity of the r_5 peak. The position of the r_4 peak stays almost the same, up to 5.4 GPa, while the position of the r_5 peak slightly decreases with increasing pressure.

Table 1 summarizes the positions of the FSDP of S(Q), the g(r) peak positions, Si-O-Si angle of MgSiO₃ glass and Si-O-Si/ Ca-O-Si angles of CaSiO₃ glass from ambient to high pressures. Since the r₃ and r₄ peaks of MgSiO₃ glass are overlapped by O-O, Si-Si, Mg-Si, and Mg-Mg distances, we carried out the multi-peak fitting procedure with the method of de Grouchy et al. (2017). We first fitted O-O, Si-Si, Mg-Si, and Mg-Mg peaks into the r₃ and r₄ peaks at ambient pressure (using the $Q_{\text{max}} = 15 \text{ Å}^{-1}$ data) by referring the bond distances and the coordination numbers reported in Ghosh et al. (2014). The g(r) at ambient pressure is well reproduced by the parameters of Ghosh et al. (2014) with minor adjustment for O-O and Si-Si distances (Online Materials1 Fig. S2a). Then, the Si-Si and Mg-Si peak positions at high pressures were determined by fixing the widths and heights of all peaks and peak positions of O-O and Mg-Mg (2.65 and 3.42 Å, respectively) (Online Materials¹ Fig. S2). It has been reported in SiO₂ glass that O-O distance does not change at least up to 6.0 GPa because of almost no change in the Si-O tetrahedron structure (Kono et al. 2022). Since our observed Si-O distances of MgSiO₃ and CaSiO₃ glasses also do not change with varying pressure (cf. Fig. 4), we assumed no change in O-O peak distance in MgSiO3 glass in the pressure range of this study up to 5.4 GPa. For Mg-Mg distances in MgSiO₃ glass, MD simulations of Salmon et al. (2019) show that the Mg-O bond distance and Mg-O-Mg angle do not change below 6 GPa, which indicates no change in Mg-Mg distance. We therefore assumed that the Mg-Mg distance has no pressure dependence in the pressure range of this study (\leq 5.2 GPa).



FIGURE 3. Position of the first sharp diffraction peak (FSDP) in S(Q) of CaSiO₃ and MgSiO₃ glasses at high pressures, compared with those of CaSiO₃ and MgSiO₃ melts reported in Funamori et al. (2004). Solid red squares and solid black triangles represent the FSDP positions of CaSiO₃ and MgSiO₃ glasses, respectively, obtained in this study. Sizes of the errors in CaSiO₃ glass results are smaller than the size of the symbol. Open red squares and open black triangles represent the FSDP positions of CaSiO₃ and MgSiO₃ melts, respectively, reported in Funamori et al. (2004). Vertical bars on the symbols represent the size of the error. Several data have the error bar smaller than the symbol size. (Color online.)

The Ca-O distances of CaSiO₃ glass at high-pressure conditions are also determined by the peak-fitting method of de Grouchy et al. (2017) because the r_3 (O-O) peak of the g(r) of CaSiO₃ glass is hidden in the right-hand-side shoulder of the r_2 (Ca-O) peak in the high-pressure data. First we fitted r_2 (Ca-O) and r_3 (O-O) peak positions at ambient pressure (using the $Q_{max} = 25 \text{ Å}^{-1}$ data) by fixing the coordination numbers reported in Mead and Mountjoy (2006b) and Bajgain et al. (2015). Our obtained Ca-O [2.302(±0.001) Å] and O-O [2.611(±0.007) Å] distances at ambient pressure are consistent with those reported in Mead

DISCUSSION

and Mountjoy (2006b) and Bajgain et al. (2015). Then, we fitted

 r_2 (Ca-O) peak positions of CaSiO₃ glass at high pressures by

fixing the coordination number and O-O peak position obtained

at ambient pressure (Online Materials¹ Fig. S3).

Figure 4 shows the nearest-neighbor Si-O and M-O (M = Mg, Ca) distances (Fig. 4a) and the intermediate range Si-Si and M-Si distances (Fig. 4b) of MgSiO3 and CaSiO3 glasses at high pressures. The Si-O peak positions of MgSiO₃ and CaSiO₃ glasses are the same, while the positions of the M-O peaks are markedly different between MgSiO₃ and CaSiO₃ glasses (Fig. 4a). The difference between Mg-O and Ca-O distances in MgSiO₃ and CaSiO₃ glasses have also been observed in previous ambient pressure studies and is considered to be due to the different ionic radius of M cations (e.g., Cormier and Cuello 2013). Our results show that the M-O peak positions of MgSiO₃ and CaSiO₃ glasses show almost no change with varying pressure. Similarly to our results, the experimental results of Salmon et al. (2019) also show almost no change in the M-O distances and coordination numbers at pressure conditions below ~5 GPa, although Salmon et al. (2019) show increase in the M-O coordination number in MgSiO₃ and CaSiO₃ glasses at pressures higher than 6 GPa. These data indicate that nearest neighbor Si-O and M-O distances do not change at pressures up to 5.4 GPa.

The intermediate range Si-Si distance of MgSiO₃ glass markedly decreases with increasing pressure (Fig. 4b), and it causes shrinking of the Si-O-Si angle $\{\theta = 2 \cdot \arcsin[(|Si - Si|/2)/|Si - O|]\}$ at high pressures (Fig. 5). It has been known that high-pressure structural changes of SiO2 glass occur mainly by decreasing the Si-O-Si angle at high pressures (e.g., Sonneville et al. 2013). Similarly to SiO₂ glass, Ryu et al. (2022) have also reported a decrease in Si-O-Si angle in MgSiO₃ glass with increasing pressure. We therefore consider that the pressure-induced structural change in MgSiO₃ glass up to 5.2 GPa is attributed to the decrease of Si-O-Si angle, the same as the well-known compression behavior of SiO2 glass (e.g., Sonneville et al. 2013). On the other hand, CaSiO₃ glass shows almost no change in the r4 peak position with varying pressure (Fig. 4), which indicates that both Si-Si and Ca-Si distances at ~3.0 Å do not change at high pressure. The calculated Si-O-Si and Ca-O-Si angles of the CaSiO₃ glass show almost no change with increasing pressure (Fig. 5), which is different from the marked decrease of the Si-O-Si angle in MgSiO₃ glass at high pressures. In exchange for the almost no change in Si-O-Si and Ca-Si-O angles, the g(r)of CaSiO₃ glass at high pressures shows a marked increase of the r₄ peak intensity accompanied by the decrease of the r₅ peak intensity (Fig. 2d). Although the r5 (Ca-Si/Ca-Ca) peak position

of Cablog glasses at ambient, and high pressure conditions						
MgSiO₃ glass	Ambient	1.0 GPa	1.9 GPa	3.0 GPa	4.3 GPa	5.2 GPa
FSDP (Å ⁻¹)	1.88(±0.01)	1.93(±0.01)	1.94(±0.01)	1.96(±0.01)	2.01(±0.05)	2.03(±0.06)
Si-O (Å)	1.621(±0.002)	1.613(±0.002)	1.618(±0.002)	1.616(±0.002)	1.605(±0.003)	1.614(±0.009)
Mg-O (Å)	2.030(±0.004)	2.026(±0.006)	2.004(±0.005)	2.050(±0.004)	2.027(±0.007)	2.055(±0.004)
0-0 (Å)	2.65(fixed)	2.65(fixed)	2.65(fixed)	2.65(fixed)	2.65(fixed)	2.65(fixed)
Si-Si (Å)	3.179(±0.006)	3.171(±0.002)	3.168(±0.002)	3.134(±0.013)	3.113(±0.003)	3.122(±0.011)
Mg-Si (Å)	3.220(±0.006)	3.226(±0.006)	3.234(±0.008)	3.210(±0.006)	3.206(±0.007)	3.209(±0.004)
Mg-Mg	3.42(fixed)	3.42(fixed)	3.42(fixed)	3.42(fixed)	3.42(fixed)	3.42(fixed)
Si-O-Si angle (°)	137.3(±0.8)	135.8(±0.5)	133.9(±0.6)	133.8(±0.6)	133.7(±0.9)	130.9(±1.4)
CaSiO₃ glass	Ambient	0.8 GPa	2.3 GPa	3.3 GPa	4.6 GPa	5.4 GPa
FSDP (Å ⁻¹)	2.137(±0.005)	2.154(±0.003)	2.168(±0.001)	2.177(±0.002)	2.189(±0.003)	2.200(±0.002)
Si-O (Å)	1.622(±0.001)	1.618(±0.003)	1.616(±0.003)	1.621(±0.003)	1.611(±0.003)	1.614(±0.003)
Ca-O (Å)	2.302(±0.001)	2.315(±0.004)	2.306(±0.004)	2.305(±0.004)	2.298(±0.004)	2.297(±0.004)
O-O (Å)	2.611(±0.007)	2.611(fixed)	2.611(fixed)	2.611(fixed)	2.611(fixed)	2.611(fixed)
Si-Si, Ca-Si (Å)	3.017(±0.008)	2.997(±0.026)	2.998(±0.032)	2.998(±0.014)	2.998(±0.018)	2.996(±0.001)
Ca-Si, Ca-Ca (Å)	3.573(±0.014)	3.569(±0.015)	3.550(±0.021)	3.557(±0.026)	3.554(±0.013)	3.554(±0.015)
Si-O-Si and Ca-O-Si angles (°)	136.8(±0.8)	135.6(±2.5)	136.2(±3.0)	135.4(±1.4)	137.0(±1.8)	136.3(±1.2)

TABLE 1. Positions of the first sharp diffraction peak (FSDP) of S(Q), peak positions in g(r), Si-O-Si angle of MgSiO₃, and Si-O-Si angles of CaSiO₂ olasses at ambient- and high-pressure conditions

of CaSiO₃ glass slightly shortens with increasing pressure (0.8% between ambient and 5.4 GPa) (Fig. 4b), it is not as large as the shortening of the Si-Si peak position in MgSiO₃ glass at high pressures (1.8% between ambient and 5.2 GPa).

These data indicate marked differences in the high-pressure behavior of intermediate range structures of MgSiO₃ and CaSiO₃ glasses. There are two important structural parameters to describe intermediate range structure in silicate glasses. One is Qⁿ species, which represents the number of bridging oxygens (n) connected with a tetrahedral cation (e.g., Mysen 1990; Stebbins et al. 1992). Salmon et al. (2019) have shown the pressure dependence of Qⁿ species in MgSiO₃ and CaSiO₃ glasses calculated by MD simulations. The MD simulations of Salmon et al. (2019) show that both MgSiO3 and CaSiO3 glasses consist of ~50% of Q2 species with ~25% of Q1 and Q3 species, which are consistent with those reported by ²⁹Si NMR measurements at ambient pressure for MgSiO₃ (Sen et al. 2009; Davis et al. 2011) and CaSiO₃ (Zhang et al. 1997; Kaseman et al. 2015) glasses. The fractions of the Qⁿ species in both MgSiO₃ and CaSiO₃ glasses show only little change with varying pressure, at least below 10 GPa (Salmon et al. 2019). The data indicate that Q^n species do not change in both MgSiO₃ and CaSiO₃ glasses, at least in the pressure conditions of this study, up to 5.4 GPa. We therefore consider that Q^n species are not the structural origin of the different high-pressure behavior of the intermediate range structures in MgSiO₃ and CaSiO₃ glasses (Figs. 4 and 5).

Another important structural parameter to describe pressureinduced structural changes in silicate glasses is polyhedron connectivity (e.g., Lan et al. 2017; Hasmy et al. 2021). It has been reported in theoretical studies that SiO_x polyhedrons of silicate glasses connect by corner-shared, edge-shared, and/or face-shared configurations, and the polyhedron connectivity may change with varying pressure (e.g., Lan et al. 2017; Hasmy et al. 2021). A molecular dynamics simulation study showed that CaSiO₃ glass has a similar polyhedron connectivity structure to wollastonite (Mead and Mountjoy 2006b). We therefore consider polyhedron connectivity in CaSiO₃ glass based on the wollastonite structure as a structural motif. In wollastonite, SiO_4 tetrahedra and CaO₆ octahedra form corner-shared SiO_4 -SiO₄ and edge-shared CaO₆-CaO₆ structures. These configurations



FIGURE 4. Peak positions in g(r) of CaSiO₃ and MgSiO₃ glasses form ambient to around 5 GPa. Red solid squares and black solid triangles represent peak positions of CaSiO₃ and MgSiO₃ glasses, respectively. Vertical bars on the symbols represent the size of the error. Several data have the error bar smaller than the symbol size. (Color online.)



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FIGURE 5. Si-O-Si angle of MgSiO₃ glasses and Si-O-Si/Ca-O-Si angles of CaSiO₃ glass as a function of pressure. The Si-O-Si angle (θ) was calculated by using simple sine relation { $\theta = 2 \cdot \arcsin[(|Si - Si|/2)/|Si - O|]$ }. Vertical bars on the symbols represent the size of the error. Several data have the error bar smaller than the symbol size. (Color online.)

yield an average Si-Si distance of 3.14 ± 0.04 Å and an average Ca-Ca distance of 3.58 ± 0.11 Å (Ohashi 1984). On the other hand, there are two Ca-Si distances in the wollastonite crystal structure formed by the corner-shared $(3.65 \pm 0.16 \text{ Å})$ and edgeshared $(3.10 \pm 0.03 \text{ Å})$ configurations of SiO₄ tetrahedron and CaO₆ octahedron (Ohashi 1984). The two Ca-Si distances of the corner-shared and edge-shared CaO6-SiO4 configurations in the CaSiO₃ structural motif correspond to the r₅ and r₄ peak positions, respectively, in CaSiO₃ glass in this study. Then, our data imply that the change of the peak intensity between the r₄ and r_5 peaks obtained in the g(r) of CaSiO₃ glass at high pressures (Fig. 2d) can be due to a structural change in the CaO₆-SiO₄ configuration. At low pressures, up to 0.8 GPa, the low r₄ peak intensity implies that the r₄ peak is mainly composed of the SiO₄-SiO₄ structure and that the fraction of the edge-shared CaO₆-SiO₄ structure is low. The low contribution of the edgeshared CaO₆-SiO₄ structure on the r₄ peak is consistent with a previous molecular dynamics simulation study of CaSiO₃ glass at ambient pressure (Mead and Mountjoy 2006b). On the other hand, at high pressures, the intensity of the r₄ peak markedly increases, accompanied by a decreasing intensity of the r₅ peak (Fig. 2d). From the previous simulation study of SiO₂ glass (Hasmy et al. 2021), the Si-Si coordination number does not change at the pressure conditions below 5.4 GPa. Furthermore, the Raman spectroscopy observations of CaSiO₃ glass below 5 GPa (Kubicki et al. 1992; Wolf and McMillan 1995) show no change in the vibrational spectra related to SiO₄ polyhedral units with increasing pressure, at least below 5 GPa, although it starts to change above 10 GPa. Therefore, we interpret the r₄ peak intensity change as the increase of the fraction of the edgeshared CaO₆-SiO₄ structure accompanied with decrease of the fraction of the corner-shared CaO6-SiO4 structure (the decrease of the intensity of the r₅ peak) at high pressures. The interpretation of the high-pressure structural behavior of CaSiO₃ glass at pressures less than 5.4 GPa is consistent with previous molecular dynamics simulations (e.g., Mead and Mountjoy 2006a; Shimoda and Okuno 2006). Mead and Mountjoy (2006a) investigated pressure-induced structural changes in CaSiO₃ glasses at 0, 5, and 10 GPa and showed that the intensity of the Ca-Si peak at ~3.1 Å increases with increasing pressure. In addition, Shimoda and Okuno (2006) also showed an increase of the Ca-Si peak at ~3.1 Å accompanied by a decrease of the Ca-Si peak ~3.6 Å between 0 and 7.5 GPa. Thus, our data suggest that compression of CaSiO₃ glass at pressures up to 5.4 GPa occurs through the modification of the CaO₆-SiO₄ structure from a corner-shared configuration to an edge-shared configuration without changing the SiO₄-SiO₄ structure.

IMPLICATIONS

In this study, we observed different structural behaviors in CaSiO₃ and MgSiO₃ glasses at high pressures. The different highpressure structural behaviors are also likely present in CaSiO₃ and MgSiO₃ melts, as Funamori et al. (2004) reported different behaviors in the FSDP position at high pressures, as seen in our observations (Fig. 3). MgSiO₃ glass shows marked shift of the position of the FSDP with increasing pressure, while CaSiO₃ glass shows only small change in the FSDP position at high pressure (Fig. 3). These data imply the possible presence of intrinsic high-pressure structural differences due to the different cations, Mg and Ca, in both silicate glass and melt, and their importance in understanding the nature and properties of silicate magmas in Earth's upper mantle. For example, it has been known that viscosity of supercooled liquid MgSiO₃-CaSiO₃ compositions shows deep minima in the viscosity-composition relationship (Neuville and Richet 1991), which is difficult to interpret by common viscosity-NBO/T [non-bridging oxygen (NBO) per tetrahedrally coordinated cation (T)] models (e.g., Bottinga and Weill 1972; Shaw 1972; Giordano and Dingwell 2003). In addition, Cochain et al. (2017) reported different high-pressure behaviors in the viscosity of MgSiO₃ and CaSiO₃ melts. CaSiO₃ melt (103.6 mPa s at 6.4 GPa and 2128 K) has markedly higher viscosity than MgSiO₃ melt (53.5 mPa s at 6.3 GPa and 2148 K) at high pressures. Furthermore, molecular dynamics simulations by Zhang et al. (2010) showed that the difference in viscosity between CaSiO₃ and MgSiO₃ melts becomes larger at 20 GPa. Our observed different high-pressure structural behavior between CaSiO₃ and MgSiO₃ glasses may be the structural origin of the marked difference in the viscosity of CaSiO₃ and MgSiO₃ melts at high pressures.

AUTHOR CONTRIBUTIONS

N.M.K and Y.K. devised the project and wrote the manuscript. N.M.K. carried out the experiments with support from Y.K., I.O., and R.H. for the experiment at the beamline 16-BM-B in APS, and Y.K., K.O., K.N., and O.S. for the experiment at the beamline BL04B2 and BL37XU in SPring-8. All authors discussed the results on the manuscript.

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Endnote:

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