Densification of MgSiO$_3$ glass with pressure and temperature

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Abstract. The density and structure of MgSiO$_3$ glass (v-En) recovered from a series of annealing experiments up to 1000ºC at 2.0, 5.5 and 8.5 GPa have been investigated using Archimedes’ method and Raman spectroscopy, respectively. The densities of recovered glasses are found to be a complex function of pressure and temperature. At room temperature, compression up to 8.5 GPa, followed by decompression, yields a glass with a density within 0.6 % of the 1-atm value. Likewise, the 1-atm density is fully recovered in glass heated up to ~500ºC at 2.0 GPa at higher pressures. A sharp increase in recovered density is observed between 500ºC and 800ºC at 2.0 GPa, 200ºC and 500ºC at 5.5 GPa and from room-T and 300ºC at 8.5 GPa. At higher annealing temperatures the changes in density are more modest. This break in slope occurs for a glass density of 2.89 g/cm$^3$ at 2.0 GPa and 2.95 g/cm$^3$ at 5.5 and 8.5 GPa. Above ~900ºC v-En crystallizes at all pressures. Raman spectra for annealed glasses show a progressive shift in the Si-O-Si bending mode to higher wave number with recovered density. From these data we estimate a ~4.5 % decrease in the Si-O-Si bond angle with densification from 2.75 g/cm$^3$ (1-atm, room T) to 3.0 g/cm$^3$.

1. Introduction

The investigation of the structure and physical properties of molten MgSiO$_3$ at high pressure offer insights into the dynamic behaviour of refractory melts in the Earth’s interior. Because of the fragile and refractory nature of MgSiO$_3$ melt, its structure and physical properties are extremely difficult to measure directly and are most commonly inferred from in-situ compression experiments at room T or ex-situ characterization of glasses heat treated and quenched from high pressure. In-situ cold compression experiments clearly demonstrate that significant structural changes occur in MgSiO$_3$ glass (v-En) compressed up to ~40 GPa, but within experimental resolution these changes are fully reversible on decompression (e.g., [1], [2]). In contrast, v-Ens compressed and heat-treated at 500ºC are found to contain appreciable 5- and 6-coordinated silicon after quenching from 10 GPa [3]. The recovery of high-coordinated silicon in compressed and heat-treated MgSiO$_3$ glasses provide a demonstration of a more general prescription for studying pressure-induced structural changes in refractory glasses and super-cooled liquids. This work follows [3] by investigating in greater detail the effects of annealing temperature and pressure on densification and structural relaxation of v-En. We also compare density and Raman data in v-En approaching and possibly exceeding glass transition temperatures to gain insight into the structural changes accommodating densification and to provide a link between glass and super-cooled liquid properties, which is important for extrapolation to higher T and P conditions.

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2. Experimental method
We used synthetic crystalline enstatite powder as the starting material. v-En was prepared by melting the enstatite powder at 1620°C in 2.0 mm (internal diameter) platinum tubing with a thin bottom and quenching the MgSiO₃ melt in air. The sample glass was cut into cylinders 2.0 mm in diameter and 2.0 mm in length (this volume corresponds to ~15 mg). High pressure and temperature relaxation experiments were performed in a Walker-style multi-anvil apparatus installed at the experimental petrology laboratory at the University of California, Davis High Pressure Laboratory. Eight one-inch tungsten carbide cubes with a 10-mm truncated edge length (TEL) were used as second anvils. The relationship between load and pressure was determined using metal-to-metal transitions of bismuth and Ba. Temperature was monitored with a C-type thermocouple, which was located 2.0-mm from the center of the sample (see paper by Gaudio et al. this volume for a complete description and discussion of the sample assembly and pressure-temperature calibrations). The peak temperature for all annealing experiments was maintained for 300 s and within 10°C. We have chosen this duration based on the characteristic relaxation time for the glass transition temperature ($T_g$). A decompression rate of ~10 GPa/min was used to decompress from all pressures for consistency since, [3] found a decompression rate dependence on structure and density of MgSiO₃ glass. The density of the recovered glasses was measured by Archimedes’ method in toluene. Density was measured ten times on all the samples to give standard deviations, and standard error for this method is ±0.01 g/cm³. Raman spectroscopy of the recovered samples has been conducted using an Ar laser (operating wave length and power are 514.5 nm and ~20 mW) installed at the Geodynamics Research Center, Ehime University.

3. Results and discussions

3.1. Crystallization temperature of MgSiO₃ glass at pressure over 300 s time scale
Partial crystallization is observed in some samples, which is unambiguously detected by optical observation because the glass showed an obvious change in color and density. The crystallized sample showed a smoky or milky color. The shift of crystallization temperature with pressure is shown in Figure 1. The crystallization temperature increases with pressure. Judging from 1 atm and 2 GPa ($T_g$ at 1 atm and 2 GPa; [4] and [5]), we may be able to assume that the crystallization temperature reflects the $T_g$s at those pressures. While we cannot confirm that any annealed glass is fully relaxed, the intervention of crystallization at the highest experimental temperatures suggest that we have exceeded glass transition temperatures in each isobaric series. Based on this assumption, the trend of the crystallization temperature indicates that the $T_g$ of MgSiO₃ glass increases with pressure. Additionally, $T_g$ tells us the viscosity of the liquid indirectly because the super-cooled liquid has ~10¹² Pa*s at the $T_g$, which does not depend on the chemical composition of the liquid. Hence, the viscosity of MgSiO₃ liquid increases with increasing pressure at least up to 8.5 GPa when the liquid MgSiO₃ is compressed isothermally. The present interpretation is consistent with predictions (e.g., [6] and [7]).

![Figure 1. Pressure dependence of the crystallization temperature of v-En. The dashed line in the figure indicates a possible crystallization temperature and is only a visual guide. $T_g$ at 1 atm and 2 GPa are taken from [3] and [4].](image-url)
3.2. Densification of v-En
The density relaxation pathways over a 300 s time-scale at a fixed given pressure is shown in Figure 2. Glasses recovered from room temperature compression results in almost no permanent densification (0.6 % densification is permanent). This advocates supporting the results of [3] which suggest that heat-treating is necessary for recovering a permanently densified glass to 1 atm. At high pressure, density increases with increasing temperature. This density relaxation pathway for v-En occurs in three stages. The first stage occurs within the low-temperature region (1). In this region, densification is almost completely reversible on decompression (the increase of the density is within 0.7 % of initial density). The second stage of density relaxation occurs in the mid-temperature region (2) where the permanent densification of recovered glasses increases abruptly. The final stage, stage 3, occurs in the high-temperature region where the density gain with increasing temperature is flat or gradual compared to region (2). As pressure increases, region (1) becomes narrower, as region (2) grows broader and shifts to lower temperature. At 8.5 GPa, region (1) finally disappears. This means the temperature of the onset of permanent density relaxation decreases with increasing pressure. The change in the slope in density vs temperature from region (2) to (3) may reflect the difference in the densification mechanism and/or mode of structural relaxation. The change in the slope of the density relaxation pathway from region (2) to (3) occurs when the density reaches to ~2.95 g/cm³. When the sample is heated to temperature above region (3) partial crystallization of sample occurs. The density of the partially crystallized glass increases abruptly (experiments indicated in Figure 2 by open symbols). The density of the crystallized glasses is close to the density of orthoenstatite (i.e., 3.22 g/cm³; [8]).

![Figure 2](image)

**Figure 2.** Density of annealed v-En at pressure and temperature. Open symbols indicate the crystallization of the samples. The error bars of the plots are from the standard deviation of each density measurements. Dashed lines in the figure are only a guide. Labelled numbers indicates the stages of the densification (see text).

3.3. Raman spectroscopy
Figures 3a and 3b show the Raman spectra of the recovered glasses (non-compressed glass and the glasses recovered from region (2) and (3) at 2, 5.5 and 8.5 GPa) and the density dependence of the position of the peak attributed to the Si-O-Si bending mode. The main peak appearing at 950 cm⁻¹ is very broad and is assigned the Q speciation of tetrahedrally coordinated Si, which consists of Q¹, Q², Q³ and Q⁴ (Qⁿ, n represents the number of bridging oxygen in the per tetrahedrally coordinated Si, e.g., [9]). The shape of this main peak shifts slightly to lower wave numbers with pressure or temperature, consistent with previous Raman studies [2]. The peak at 950 cm⁻¹ consists of two peaks from Q² (~970
cm\(^{-1}\)) and Q\(^1\) (~900 cm\(^{-1}\)) speciation. In the mid-frequency region, there is a small peak ~650 cm\(^{-1}\). This peak has been assigned to the bending mode of Si-O-Si in a silicate glass (e.g., [10]). The peak position shifts to higher wave numbers with increasing density as shown in Figure 3(b). By combining the high-pressure Raman studies and theoretical calculation by [1] and [10] the decrease in average Si-O-Si bond angle can be calculated from the peak position. These studies suggest that the Raman band assigned to the Si-O-Si bending mode increases 60 cm\(^{-1}\) for 15\(^\circ\) of bond angle compression (4 cm\(^{-1}/\text{\(^\circ\)}\)). From our Raman data we estimate a ~4.5 % reduction in the average intertetrahedral bond angle. However, we cannot find a striking structural change by the present Raman spectroscopy that reflects the trend of the density change with temperature reported in the last section. The molecular dynamics simulation by [7] suggests ~5 % angle reduction when the density of the glass reaches to 3.00 g/cm\(^3\). Additionally, in their prediction, ~4 % of highly coordinated Si (specifically 5-coordinated Si) appears when the density of glass reaches to 3.00 g/cm\(^3\). This prediction is also consistent with the \(^{29}\)Si MAS NMR study by [3] which suggests that ~4.5 % of Si is highly coordinated (5- and 6-coordinated Si) in densified v-En with a density of 3.03 g/cm\(^3\). When this result is considered together with the studies of [7] and [1], it can be suggested that the onset of increasing Si coordination during densification of v-En occurs at a density below, but near 3.00 g/cm\(^3\). In the present study, samples recovered from 5.5 GPa at temperatures above 500°C have densities within 0.05 g/cm\(^3\) of 3.00 g/cm\(^3\), and if the onset of increasing Si coordination is density dependent, then a small (~1-2 %) proportion of 5-coordinated Si may be present in more fully relaxed samples at 5.5 GPa.

Figure 3. (a) An example of Raman spectra of the recovered glasses. Blue and red patterns indicate the spectra of the glasses recovered from the regions (2) and (3), respectively (At 2 GPa, change the figure so that the lower temperature experiment is shown first). The small sharp peaks in the spectra are from a cosmic ray during the measurements. (b) The relationship between density and Raman shift of the peak from the Si-O-Si bending mode.

4. Conclusion
In this paper, we have presented the density change and structure of relaxed MgSiO\(_3\) glass (v-En) by ex-situ high-pressure and high-temperature experiments. The density relaxation pathway has a similar trend at all pressures. The crystallization temperature of v-En increases slightly with pressure. We described regions where the recovered glass density increases steeply with temperature and where the density increases gradually with temperature. The boundary between regions (2) and (3) occurs at a
density located on the boundary of ~2.95 g/cm$^3$ at pressures of 5.5 and 8.5 GPa. The change in the trend of densification with temperature may be able to be explained by as a change in the mechanism of the structural modification. The estimated reduction of the Si-O-Si bond angle from Si-O-Si bending mode in the Raman spectra is ~4.5 %, which is consistent with previous prediction (~5 % at 3.00 g/cm$^3$).

5. References
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