Stability and crystal structure of $MgSiO_3$ perovskite to the core-mantle boundary

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[1] We report in situ angle-dispersive X-ray diffraction measurements for $MgSiO_3$ at 90–118 and 135–144 GPa and 300–2900 K. At 90–144 GPa, we observed a new diffraction peak at 2.57–2.62 Å as reported in *Shim et al.* [2001]. The pressure-induced position shift of the new peak is consistent with those of $MgSiO_3$ perovskite (Mg-Pv), supporting that the new peak is associated with a modification in crystal structure of Mg-Pv at 88 GPa. During laser heating above 2500 K at 144 ± 10 GPa, in addition to peaks of Mg-Pv, we observed new peaks as well as peak splittings and intensity changes of some peaks. The major features in the diffraction patterns can be explained by the modified Mg-Pv proposed by *Shim et al.* [2001] together with the post-perovskite phase proposed by *Murakami et al.* [2004]. This supports the existence of a major phase transition in $MgSiO_3$ under conditions close to those at the base of Earth's mantle. *INDEX TERMS:* 3924 Mineral Physics: High-pressure behavior; 3954 Mineral Physics: X ray, neutron, and electron spectroscopy and diffraction; 8124 Tectonophysics: Earth's interior—composition and state (1212). **Citation:** Shim, S.-H., T. S. Duffy, R. Jeanloz, and G. Shen (2004), Stability and crystal structure of $MgSiO_3$ perovskite to the core-mantle boundary, *Geophys. Res. Lett.*, *31*, L10603, doi:10.1029/2004GL019639.

1. Introduction

[2] Knowledge about physical properties and stability of $MgSiO_3$ perovskite (Mg-Pv), the dominant mineral in the lower mantle, is fundamental to understanding the structure and chemical composition of the region. Nevertheless, the stability of Mg-Pv has been a subject of controversy [*Meade et al.*, 1995; *Saxena et al.*, 1996; *Serghiou et al.*, 1998]. The most recent studies under stable heating conditions (i.e., argon insulation media) [*Fiquet et al.*, 2000; *Shim et al.*, 2001] have not extended beyond 2200-km depth conditions. Moreover, recent seismological studies have documented changes in the structure and dynamics of the lowermost

mantle [e.g., *van der Hilst and Kárason*, 1999; *Lay et al.*, 1998]. Thus, it is of great interest to examine the stability and possible structure changes of Mg-Pv at these depth conditions. In fact, the most recent studies have proposed a modification of the perovskite structure at 88 GPa [*Shim et al.*, 2001] and a post-perovskite transition to a *Cmcm*-type structure at 120 GPa [*Murakami et al.*, 2004]. In this paper, we report in-situ angle-dispersive X-ray diffraction measurements at 90–118 and 135–144 GPa and 300–2900 K. Possible phase changes in $MgSiO_3$ will be discussed.

2. Experimental Techniques

[3] $MgSiO_3$ glass mixed with 10 wt% platinum powder was used as a starting material as in *Shim et al.* [2001]. A 10-μm thick sample foil was loaded in a 50-μm diameter hole in a 25-μm thick indented Re gasket. Argon was cryogenically loaded with the sample foil as both pressure transmitting and insulating medium. The foil was separated from the diamonds by placing 1–3-μm diameter sample chips below and above the foil. The sample was compressed by 100-μm beveled anvils in a symmetric diamond cell.

[4] Angle-dispersive diffraction was conducted at the GSECARS sector of the Advanced Photon Source using a 1024 × 1024-pixel CCD detector. Diffraction patterns of CeO_2 were measured to correct for tilting of the detector and to calibrate sample-to-detector distance. A 11 × 11 μm² monochromatic (29.2 keV) X-ray beam was focused on the samples. In order to detect high-angle diffraction peaks, we tilted the diamond cell by 4° with respect to the incident X-ray beam. This limits diffraction peak integration to only 180° of the ring (Figure 1), but still constrains diffraction intensities much better than our previous energy-dispersive diffraction study [*Shim et al.*, 2001]. The CCD images were integrated to 1D patterns using the program Fit2d [*Hammersley*, 1997].

[5] A double-side laser heating system (Nd:YLF in TEM_{01} mode) [*Shen et al.*, 2001] was used to heat the samples over 1500 K for 30–45 minutes. Temperature was measured from one side only. Including radial thermal gradients and temporal fluctuations during the X-ray expo-
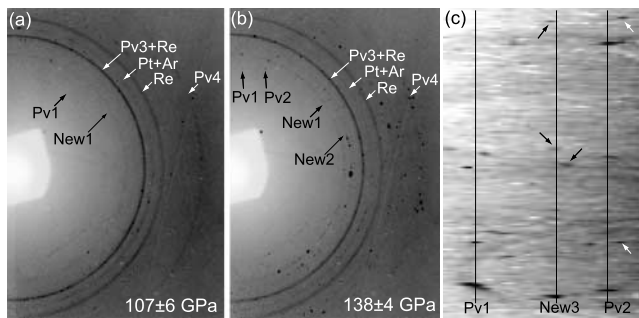
Figure 1. X-ray diffraction images of the samples at **(a)** 107 and **(b)** 138 GPa measured after heating. **(c)** A section (7–9°2θ) of an unrolled projection of (b) along an azimuthal line (x- and y-axes are in diffraction and azimuthal angle scales, respectively). Peak assignments are shown for major diffraction rings (Ar: argon pressure medium, Pt: platinum laser absorber, Re: rhenium gasket). "Pv1", "Pv2", "Pv3", and "Pv4" indicate a doublet (002 + 110), a singlet (111), a triplet (020 + 112 + 200), and a doublet (103 + 211), respectively, which are diagnostic diffraction features of perovskite. "New1", "New2", and "New3" refer to the observed new peaks. The vertical lines in (c) are to guide the eye. New3 and a new peak observed near Pv2 are indicated by black and white arrows, respectively.

sure, the temperature (T) uncertainty is estimated to be 100–300 K.

[6] Pressure was measured using the equations of state (EOS) of Pt [*Holmes et al.*, 1989] and Ar [*Ross et al.*, 1986]. Due to peak overlap between Pt and Ar, the uncertainty in pressure (P) is ±5 GPa at 300 K. Including temperature uncertainties of 300 K, the uncertainty in pressure at high T is typically ±10 GPa. Pressure calculated from the EOS of Mg-Pv [*Jackson and Rigden*, 1996] shows agreement within the estimated uncertainty. For phase identification, we calculated diffraction patterns of MgSiO₃, MgO, SiO₂, Re, Pt, and Ar, using the published EOSs and structural parameters given in *Shim et al.* [2001].

3. Results

[7] Our data examine the stability and the crystal structure of MgSiO₃ to core-mantle boundary (CMB) conditions (Figure 2). Before heating, we only observe diffraction peaks from the Re gasket, Pt, and Ar, because the starting material is amorphous (Figure 3a). During heating, diffraction peaks identified as those of Mg-Pv appeared. At least six of the dominant peaks show agreement with the calculated peak positions of Mg-Pv. In the images, the diffraction peaks of Mg-Pv appear as spotty rings (Figure 1). The most intense peak of Mg-Pv (triplet, Pv3) overlaps a Re gasket diffraction peak. However, two of the triplet peaks are observed on the shoulder of the Re peak. Pv4 (doublet) is clearly observed throughout our experiments. Pv2 (singlet) is very weak and is much less frequently resolved. However, because it has zero intensity for cubic perovskite (Pv), it can be used to identify non-cubic Pv. Subsequent heating cycles were performed at higher P for the Mg-Pv sample synthesized during the first heating cycle (Figures 3b and 3c). Some of our new data were measured

at higher T (>2500 K) at 100–120 GPa than those of our previous data [*Shim et al.*, 2001]. These T conditions are comparable to those of a previous study at somewhat lower P [*Saxena et al.*, 1996] that suggested a dissociation of Mg-Pv. Our results thus demonstrate that these observations are not due to higher T achieved. A phase transition to a cubic structure has been proposed at 65 GPa [*Meade et al.*, 1995]. The existence of shoulder peaks of the triplet and Pv2 rules out the possibility of a transition to a cubic structure at 100–144 GPa.

[8] *Shim et al.* [2001] reported a new peak at 2.62 Å appearing above 88 GPa during heating. This peak is also observed in this study (New1 in Figures 1 and 3). Whereas the peak appeared in 50% of measured patterns in our previous report, this peak was found in all patterns in our new measurements. The fact that angle-dispersive diffraction used here covers 180° of diffraction rings, whereas the previous report was based on the energy-dispersive method which only covers a few degrees of the rings, suggests that the previous observation is due to preferred orientation. This peak cannot be attributed to those of any known or postulated structures of MgO, SiO₂, Pt, Re, or Ar. The association of this new peak with Mg-Pv was proposed based on the fact that the peak can be indexed as 012 of the *Pbnm* Pv structure. However, the 012 peak is predicted to have zero intensity for the *Pbnm* structure, and a modification of the Mg-Pv structure needs to be invoked in order to obtain the observed intensity: *P2₁/m* (monoclinic), *Pmmn* (orthorhombic), or *P4₂/nmc* (tetragonal) [*Shim et al.*, 2001].

[9] Our new data cover 90–140 GPa at 300 K, which is sufficient to examine the pressure-dependence of the New1 position (Figure 4). The peak overlaps between the triplet (Pv3) and Re hinders us from obtaining reliable unit-cell parameters for Mg-Pv directly from our patterns. Instead, we calculate the expected peak positions by extrapolating the elasticity and unit-cell parameters measured below 80 GPa. Because the long extrapolation of the linear axial compressibility results in error, we first calculated the unit-cell volumes from the EOS of Mg-Pv [*Jackson and Rigden*,
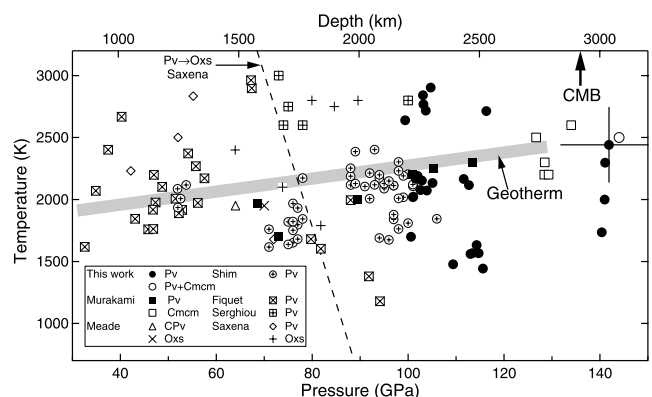

Figure 2. P-T conditions for the data points reported for the stability of Mg-Pv [*Meade et al.*, 1995; *Saxena et al.*, 1996; *Fiquet et al.*, 1998, 2000; *Serghiou et al.*, 1998; *Murakami et al.*, 2004]. A representative error bar (1σ) of our data is shown. P-T conditions for the proposed dissociation of Mg-Pv is shown as a dashed line [*Saxena et al.*, 1996]. The geotherm is from *Brown and Shankland* [1981].
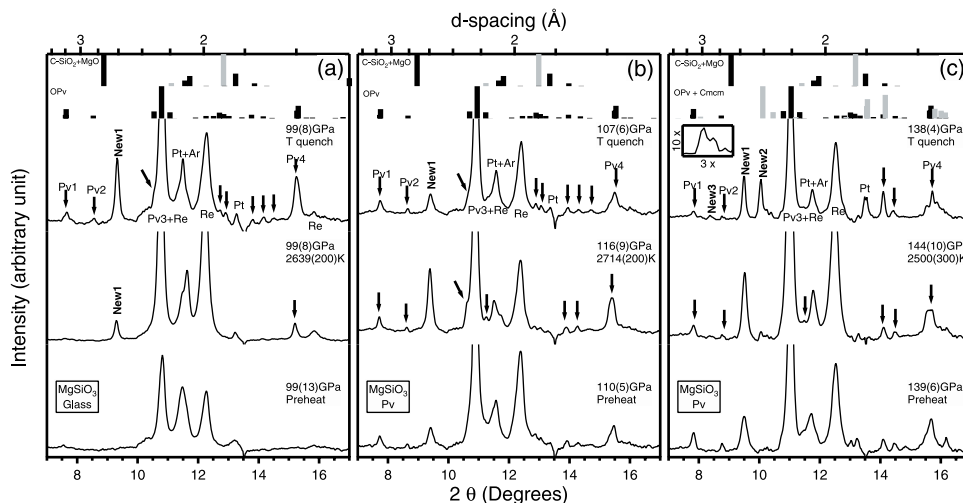
Figure 3. Integrated X-ray diffraction patterns at the indicated P-T conditions (the numbers in the parentheses are 1σ uncertainties). **(a)** MgSiO₃ glass → Mg-Pv + New1. **(b)** Mg-Pv → Mg-Pv + New1. **(c)** Mg-Pv → Mg-Pv + New1 + post-Pv. The backgrounds are subtracted. Calculated patterns for *Pbnm* Mg-Pv (black bars), *Cmcm*-type structure (grey bars), periclase (grey bars), and CaCl₂-type SiO₂ (black bars) are shown at the top. The major diffraction peaks of MgSiO₃ are identified with arrows. The inset in **(c)** shows the observed peak splitting of Pv2. Other notations are the same as those in Figure 1.

1996] and calculate the unit-cell parameters using the expected axial ratios from the axial compressibility [*Fiquet et al.*, 2000].

[10] The observed pressure-induced shifts of Mg-Pv diffraction peaks are consistent with the predicted positions at high P within mutual uncertainties. The degree of agreement between New1 and the expected d-spacings for 012, which is the closest diffraction peak in Mg-Pv, is comparable to that of other Mg-Pv diffraction peaks. Thus, this observed agreement over a 50 GPa range supports the association of the new peak with Mg-Pv or another material with very similar compressibility.

[11] In order to distinguish among the three possible Pv structures, measured intensities can be compared with expected peak intensities. The intensity of New1 is comparable to that of Pv4 with an intensity ratio of 1.3 ± 0.3 and insensitive to P,T change. However, limitations arise from the fact that the geometric model we used [*Shim et al.*, 2001] does not provide constraints for the Mg position shift nor the distortion of the SiO₆ octahedra. Furthermore, the overlap of Pv3 and Re peaks prevents us from performing Rietveld analysis. The reflection conditions for the proposed space groups show that New1 is particularly sensitive to the Mg and O positions for *P4₂/nmc* and *Pmmn*, and moderately sensitive for *P2₁/m*. However, the occasional appearance of both shoulder peaks in the triplet during heating is inconsistent with the *P4₂/nmc* structure, which is expected to show only a doublet.

[12] During heating at 135–145 GPa, temperature was held below 2500 K for first the 20 minutes. Mg-Pv peaks together with New1 were obtained at this condition. When the sample was heated above 2500 K at 144 ± 10 GPa (open circle in Figure 2), three new peaks appeared (2.42 Å New2; 2.93 Å New3; 2.75 Å near Pv2 in Figures 1b, 1c and 3c), while the major diffraction peaks of Mg-Pv and New1 are still retained. These new features are also observed after temperature quench. None of MgO, SiO₂,

Pt, Re, and Ar diffraction can explain the appearance of these peaks. Furthermore, none of the proposed structures above 88 GPa have diffraction peaks near New2 and New3. However, the peak at 2.75 Å can be interpreted as a result of peak splitting of Pv2 (Figure 1c). In fact, all the proposed structures for the change at 88 GPa predict the splitting of Pv2. One possible interpretation is that the degree of splitting becomes sufficient only above 140 GPa for the splitting to be resolved. Annealing of stresses by heating may also play an important role. New3 appears as a few weak dots in diffraction images and is at least a doublet (Figure 1c). In addition, the two peaks at 14–15° and the two peaks at the higher angle side of Pv4 become more intense. Also a peak at 13.7° appears. This could be associated with the Pt 200 reflection but this peak has not
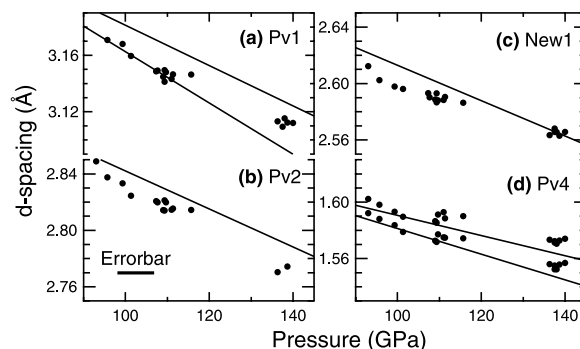

Figure 4. Measured d-spacings (solid circles) of Mg-Pv at 300 K. For comparison, the expected d-spacings of Mg-Pv with *Pbnm* space group are calculated (solid lines). Because the peak splitting for Pv1 is not well resolved, we fit the diffraction peak to a single peak **(a)**. Clear peak splittings are observed for Pv4 **(d)**. A representative error bar (1σ) is shown in **(b)**. Solid lines are the expected d-spacing changes at high P using the measurements by *Fiquet et al.* [2000].

been observed with such strong intensity (relative to Pt 111) in other patterns (Figure 3). Also, the width of this peak is about 50% broader than other peaks.

[13] In order to explain New2 and New3, we have applied the same approach we used in *Shim et al.* [2001]. However, none of the Pv structures induced by simple tilting of octahedra can explain these peaks. We also calculated expected diffraction patterns of the recently proposed post-perovskite (post-Pv) structure [*Murakami et al.*, 2004] (grey bars in Figure 3c). New2 shows good agreement with the most intense peak of the post-Pv structure. Also, the appearance of weak peaks at the higher angle side of Pv4 and at 13.7°, and the intensity increases in the peaks at 14–15° are consistent with the post-Pv structure. However, New1 and New3 cannot be explained by the post-Pv structure. The observed patterns with diffraction peaks of Mg-Pv and several new features may indicate an incomplete transition from modified Mg-Pv to the post-Pv phase. In addition, the fact that only Mg-Pv (with New1) is observed below 2500 K after 20 minutes of heating may indicate that Mg-Pv is still stable at temperatures below 2500 K at CMB pressures.

4. Discussion

[14] We have observed X-ray diffraction peaks characteristic of MgSiO$_3$ perovskite (Mg-Pv) at 90–118 and 135–144 GPa and 300–2900 K. One possible interpretation for the discrepancy among previous experiments regarding the stability of Mg-Pv has been steep thermal gradients in the sample. In one of our patterns recorded upon quench at an area 10 μm away from the hot spot, where thermal gradient is high, at 107 GPa, we found a weak peak which can be assigned to the most intense peak of the CaCl$_2$-type silica phase.

[15] The appearance of a new peak at 88 GPa (New1) [*Shim et al.*, 2001] is confirmed and its observation extended to our highest pressures. Our new data also enable association of New1 with a modification in Mg-Pv because the observed shifts in d-spacing are consistent with other major Mg-Pv diffraction peaks. However, other studies performed at similar P-T conditions have not reported such changes [*Serghiou et al.*, 1998; *Fiquet et al.*, 2000; *Andrault*, 2001; *Murakami et al.*, 2004]. Although we discussed this discrepancy in *Shim et al.* [2001], there are some other issues that need to be addressed. The observed Re peaks are not diffracted from the incident X-ray beam, whose size (11 × 11 μm^2) is still smaller than the sample chamber (20 × 50 μm^2). The peak was diffracted by the X-rays scattered at the beam-defining slits which are located at 10 cm in front of the sample. Due to the higher density and X-ray scattering cross section of Re, these weak X-rays can give rise to strong diffraction from Re which is 10–30 μm away from the X-ray center.

[16] Reaction between the sample and Re could result in the formation of Re-silicate or oxide during heating. In fact the laser beam size (20 μm) focused on the sample surface is comparable to the size of the sample chamber. However, we observed no significant thermal radiation from the gasket adjacent to the sample. Thus, the temperature of gasket should be below 1000 K which is low to drive a chemical reaction.

[17] If the new peak is due to the diffraction from the product of a chemical reaction, the material should show additional diffraction peaks. Even the simplest structured solids, such as Ar or Pt with face-centered cubic structure, have more than two strong diffraction peaks. However, New1 is the only new feature identified at 88–118 GPa and our measurements of 2D images rule out the presence of an impurity with high preferred orientation. Due to the limited knowledge about the chemical behavior of Re at these extreme conditions, the possible association of New1 with a chemical reaction remains speculative.

[18] Recently *Murakami et al.* [2004] have reported X-ray measurements of MgSiO$_3$ at 68–134 GPa and 1700–2600 K (Figure 2). They do not observe the New1 peak. It is worth pointing out that no insulation medium was loaded and only a gel starting material was used, whereas we have used Ar as an insulation medium and confirmed the presence of the New1 peak above 88 GPa using crystalline, amorphous, and oxide mixture starting materials [*Shim et al.*, 2001].

[19] Another change in diffraction pattern was observed at 144 ± 10 GPa and 2500 K while major Mg-Pv diffraction peaks remained. We found that an intense new peak (New2) is consistent with the expected major peak of the post-perovskite (post-Pv) structure [*Murakami et al.*, 2004]. While both structures have a peak near 14.0°, the intensity increase is more consistent with that expected for the post-Pv phase. Also, the large broad peak observed near 13.7° may be compatible with the post-Pv phase. The broad structure observed around Pv4 is also markedly different from our lower P observations, and is consistent with a mixture of the two phases. Thus, the observed patterns at this condition can be explained by the modified Mg-Pv [*Shim et al.*, 2001] together with the post-Pv phase [*Murakami et al.*, 2004]. Use of an Ar insulation medium in our measurements supports that the phase transition is not induced by thermal instability or gradient. This supports the existence of a major phase transition in MgSiO$_3$ under conditions close to those at the base of Earth's mantle.

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