

Reinvestigation of the MgSiO₃ perovskite structure at high pressure

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ABSTRACT

High-pressure single-crystal X-ray diffraction experiments of MgSiO₃ perovskite have been carried out up to 15 GPa in a diamond-anvil cell using synchrotron radiation. Precise crystal structural parameters, including the anisotropic displacement parameters of every atom in MgSiO₃, are determined under high pressure. In the pressure range up to 15 GPa, the most important responses of the structure are the compressions of SiO₆ and MgO₈ polyhedra and an increase in tilting of SiO₆ octahedra represented by the decrease in angles between octahedra (both Si-O2-Si angle in the *a-b* plane and Si-O1-Si angle in the *b-c* plane decrease). The degree of the change in both angles in the *a-b* and *b-c* planes is the same. The amplitude of mean square displacement for the Mg atom has the largest value in the structures and its thermal vibration is significantly anisotropic at ambient pressure. Under high pressure, all atoms in the structure have obvious anisotropy of thermal vibration and the largest amplitudes of thermal vibration for Mg, Si, and O2 atoms are directed toward vacant space in the structure. Anisotropy of the structure increases with pressure.

Keywords: Crystal structure, high-pressure study, MgSiO₃ perovskite, pressure responses, thermal vibration

INTRODUCTION

High-pressure modifications of magnesium silicates are the most important end-members of the mineral assemblage in the Earth's mantle. A detailed knowledge of their structures is therefore of great importance, not only for high-pressure crystal chemistry, but also for understanding the Earth's mantle. The perovskite-type MgSiO₃ was predicted to be an important mineral phase in the Earth's lower mantle (Reid and Ringwood 1975). Fiquet et al. (2000) determined the atomic coordinates of perovskite-type MgSiO₃ under high pressure and high temperature by the Rietveld method. They reported that distortion of the framework formed by the linkage of SiO₆ octahedra, detected by changes in the Si-O-Si angles, increased with increasing pressure and decreased with increasing temperature, and that the pressure effect on the distortion is much larger than the temperature effect. The investigation of the crystal structure of MgSiO₃ perovskite under high pressure is, therefore, important even at room temperature.

The previous crystal structure analyses of single-crystal MgSiO₃ perovskite under high pressure and room temperature using sealed tube X-ray sources (Kudoh et al. 1987; Ross and Hazen 1990) did not use sufficient number of reflections in comparison with the number of refined structural parameters to refine

the anisotropic displacement parameters. In this study, precise crystal structural parameters based on the anisotropic thermal vibration model of atoms are determined under high pressure, and the structural variation of MgSiO₃ perovskite up to 15 GPa is discussed based on a single-crystal X-ray diffraction experiment using a diamond anvil cell and synchrotron radiation.

EXPERIMENTAL METHODS

Single crystals of MgSiO₃ perovskite were synthesized from a mixture of SiO₂ and Mg(OH)₂ at 25 GPa and 1650 °C with a heating duration of 3.5 h. The analytical results of an electron microprobe analyzer gave a chemical composition of 40.0(4) wt% MgO, 59.2(5) wt% SiO₂, and 0.5(1) wt% Cr₂O₃, with a total of 99.7. IR spectroscopy was carried out to determine the contents of hydroxyl-group in the run products. No significant peaks for hydroxides or hydroxyl were observed in the crystals of MgSiO₃ perovskite.

Un-twinned single-crystal specimens were selected by precession photographs. A Merrill-Bassett-type diamond-anvil cell equipped with a beryllium backing plate was used as a pressure cell. The samples, together with ruby chips and a 16:3:1 mixture of methanol:ethanol:water were loaded into a 260 μm diameter hole within a 200 μm thick steel gasket pre-indented to 75 and 65 μm for 7.5 and 10 GPa experiments, respectively. For the 15 GPa run, a 250 μm thick Re gasket pre-indented to 85 μm was used. The culet size was 500 μm. Measurements were carried out after pressure was kept for three days. Pressure was measured using the pressure dependence of ruby fluorescence with an estimated accuracy of less than 0.1 GPa. Pressure was measured in seven points around the sample. Measured pressure corresponded in the range of the error at 7.8 and 10 GPa, but the difference in maximum 0.4 GPa was recognized as each pressure at 15 GPa.

Ambient pressure data were collected using a RIGAKU AFC5S four-circle diffractometer with graphite-monochromatized MoK α radiation ($\lambda = 0.71069$ Å).

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High-pressure single-crystal X-ray diffraction measurements were carried out at 7.8, 10.0, and 15.0 GPa with a four-circle diffractometer at the BL-10A beam line of the Photon Factory (Tsukuba, Japan), using monochromatized X-ray ($\lambda = 0.70063 \text{ \AA}$). The beam size was 1 mm ϕ and a scintillation detector was used. A different crystal used at each pressure point because of a restriction of the beam time in the synchrotron facility. Absorption by the diamond-anvil cell was corrected analytically. The structural parameters at ambient condition by Horiuchi et al. (1987) were used as the initial values for the present refinements. The refinements were carried out with the least-squares program RADY89 (Sasaki 1989). Throughout the computations, the ionic form factors for Mg²⁺, Si⁴⁺, and O²⁻ as given in the *International Tables for X-ray Crystallography* (1974) were used. The final R-factors and refined structural parameters are listed in Tables 1, 2, and 3.

RESULTS AND DISCUSSION

In Table 1, the lattice constants agree well with the previously reported values (Ross and Hazen 1990). For easier comparison with cubic perovskite, the orthorhombic lattice constants *a*, *b*, and *c* can be represented as pseudo-cubic axes. We find $a' = 3.334 \text{ \AA}$, $b' = 3.446 \text{ \AA}$, and $c' = 3.402 \text{ \AA}$ at 10 GPa with $a' = a/\sqrt{2}$, $b' = b/\sqrt{2}$ and $c' = c/2$. The linear axial compressibilities decrease in order of c' , a' , and b' ; the longest axis b' is the stiffest. Thus, the degree of orthorhombic distortion of the lattice increases with pressure (Table 4).

Table 5 lists the calculated inter-atomic distances and bond angles. The polyhedral bulk modulus for SiO₆ octahedron [310(20) GPa] is smaller than the previously reported values (380 GPa—Kudoh et al. 1987; 333 GPa—Ross and Hazen 1990). The value for the MgO₈ polyhedron [270(20) GPa] is larger than that found in the literature (190 GPa—Kudoh et al. 1987). Cell volume ($V_{\text{SiO}_6} - V_{\text{MgO}_8}$), tolerance factor, and bond length distortion factors ($\Delta_{\text{B-site}}$) are listed in Table 6.

Ross and Hazen (1990) reported that the SiO₆ octahedra begin to tilt above 5 GPa and tilt angles change rapidly before 10.6 GPa, however, such behavior is not observed in this study (Fig. 1). This discrepancy is probably due to the difference in analytical precision between the two studies; our results should be more reliable than the previous studies because a larger number of reflections was used in the present refinements. In the pressure range up to 15 GPa, the most important responses of the structure are the compressions of SiO₆ and MgO₈ polyhedra and an increase in tilting of SiO₆ octahedra represented by the decrease in angles between octahedra (Si-O2-Si and Si-O1-Si). The degree of the change in both angles in the *a-b* and *b-c* planes is the same. These variations occur gradually and smoothly. These variations are consistent with that by Fiquet et al. (2000) who reported a pressure-induced increase in distortion as characterized by the Si-O2-Si angles (Fig. 1). Distortions of MgSiO₃ perovskite under lower mantle conditions could be extrapolated from the results obtained at these lower pressures.

The anisotropic displacement parameters, U_{ij} , in MgSiO₃ perovskite are given in Table 3, together with those of the orthorhombic (*Pbnm*) perovskite-type calcium titanate and germanate.

TABLE 1. Crystallographic data and data collection parameters

Pressure (GPa)	0.0001	7.8	10.0	15.0
Sample size (μm^3)	60×40×40	60×40×30	80×60×40	40×40×20
<i>a</i> (\AA)	4.7781(8)	4.722(3)	4.7148(7)	4.701(9)
<i>b</i> (\AA)	4.9305(11)	4.880(6)	4.8741(9)	4.870(4)
<i>c</i> (\AA)	6.8990(9)	6.825(4)	6.8051(8)	6.782(7)
<i>V</i> (\AA^3)	162.53(5)	157.2(4)	156.38(4)	155.2(4)
Density(g/cm ³)	4.103	4.240	4.264	4.296
Scan type	ω -2 θ	ω	ω	ω
Scan speed($^\circ$ /min)	1	1	1	1
2 θ range	10<2 θ <120	10<2 θ <86	10<2 θ <87	10<2 θ <89
Range of <i>hkl</i>	0< <i>h,k,l</i> <11,11,16	0< <i>h,k,l</i> <9,6,10	0< <i>h,k,l</i> <7,7,11	0< <i>h,k,l</i> <5,8,12
<i>R</i> (%)	3.14	4.29	4.34	5.18
<i>wR</i> (%)	3.07	5.39	6.02	6.31
GoF	1.86	0.92	1.96	1.54
No. of meas. Ref	1633	309	438	163
No. of independ. Ref with $ F_o > 3\sigma F_o $	498	233	277	132

Note: Weighting scheme = $1/(\sigma(|F_o|)^2 + (\text{Rint} * |F_o|)^2)$.

TABLE 2. Refined positional parameters and equivalent isotropic displacement parameters for perovskite-type MgSiO₃

Pressure (GPa)	0.0001	7.8	10.0	15.0
Mg <i>x</i>	0.5141(3)	0.5152(2)	0.5153(3)	0.5196(11)
<i>y</i>	0.5560(2)	0.5585(4)	0.5582(3)	0.5590(5)
<i>z</i>	1/4	1/4	1/4	1/4
B_{eq} or B_{iso} (\AA^2)	0.47(2)	0.43(4)	0.36(4)	0.38(6)*
Si <i>x</i>	1/2	1/2	1/2	1/2
<i>y</i>	0	0	0	0
<i>z</i>	1/2	1/2	1/2	1/2
B_{eq} or B_{iso} (\AA^2)	0.27(1)	0.21(3)	0.24(3)	0.27(4)*
O1 <i>x</i>	0.1018(4)	0.1040(4)	0.1034(6)	0.1046(20)
<i>y</i>	0.4665(4)	0.4646(4)	0.4655(5)	0.4679(10)
<i>z</i>	1/4	1/4	1/4	1/4
B_{eq} or B_{iso} (\AA^2)	0.31(4)	0.25(6)*	0.29(8)	0.41(10)*
O2 <i>x</i>	0.1962(3)	0.1926(7)	0.1945(4)	0.1933(13)
<i>y</i>	0.2013(3)	0.2012(9)	0.2000(4)	0.2003(8)
<i>z</i>	0.5526(2)	0.5531(2)	0.5533(2)	0.5536(6)
B_{eq} or B_{iso} (\AA^2)	0.38(3)	0.28(4)*	0.30(5)	0.39(7)*

* Isotropic displacement parameter.

The displacement parameters, corresponding to the mean square displacement, can provide much useful information on thermal properties of minerals such as Debye-characteristic temperature, anharmonicity of thermal vibration, thermal expansion, effective potential, and diffusion path (Willis and Pryor 1975; Yoshiasa et al. 1987, 1997). The displacement parameter includes the effects of both static and dynamical disorders; the former is the configuration disorder, while the latter arises from thermal vibrations of atoms. The contribution of the thermal vibration to the displacement parameters can be extracted from temperature dependence of the parameters (Yoshiasa et al. 1987, 1999), and thus temperature dependence experiments are necessary for the quantitative interpretation of thermal vibration. Though the detailed research on temperature dependence of Debye-Waller factors for these compounds is now in progress, some tendencies on thermal vibration of atoms in perovskite-type structure can be found from Tables 2 and 3. At ambient pressure, it seems that the amplitudes of U_{33} and U_{22} are the largest for Mg and Ca, respectively, and that the amplitude of U_{33} is the smallest for the octahedral site. In particular, it is an important thermal property at the atomic level for the perovskite structure that the equivalent isotropic displacement parameters, B_{eq} , for Mg and Ca atoms are larger than those for oxygen atoms. These amplitudes of thermal vibration are the largest in the structure. It is known from the EXAFS experiments (Yoshiasa et al. 2001) that the

TABLE 3. Anisotropic displacement parameters ($\times 10^4 \text{ \AA}^2$) for atoms in CaGeO₃ and CaTiO₃ perovskites at 0.1 MPa and MgSiO₃ perovskite at 0.1 MPa, 7.8 GPa, and 10 GPa

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
CaTiO₃						
	0.1	MPa	Buttner and Maslen (1992)			
Ca	81(1)	90(1)	87(1)	-16(1)	0	0
Ti	59(1)	57(1)	43(1)	-0(1)	1(1)	3(1)
O1	92(4)	107(4)	35(3)	-7(3)	00	
O2	73(2)	74(2)	91(2)	-26(2)	5(2)	-11(2)
CaGeO₃						
	0.1	MPa	Sasaki et al. (1983)			
Ca	64(3)	93(3)	84(3)	3(3)	0	0
Ge	29(1)	35(1)	28(1)	0(1)	-0(1)	-0(1)
O1	50(10)	93(11)	43(11)	6(8)	0	0
O2	69(7)	68(7)	67(6)	-22(7)	2(6)	34(6)
MgSiO₃						
	0.1	MPa	Horiuchi et al. (1987)			
Mg	52(2)	56(2)	62(1)	5(2)	0	0
Si	34(2)	37(1)	24(1)	0(2)	0(1)	-2(1)
O1	43(4)	58(4)	22(2)	1(3)	0	0
O2	43(2)	45(3)	43(1)	8(2)	5(2)	8(2)
MgSiO₃						
	0.1	MPa	This study			
Mg	58(4)	52(3)	69(2)	6(4)	0	0
Si	35(2)	34(2)	32(1)	-4(3)	-3(2)	-1(1)
O1	37(5)	37(6)	45(3)	0(4)	0	0
O2	47(4)	50(4)	48(2)	4(3)	6(3)	3(3)
MgSiO₃						
	7.8	GPa	This study			
Mg	47(4)	39(5)	78(7)	9(3)	0	0
Si	17(8)	36(3)	30(6)	1(2)	1(2)	-7(2)
O1*	32(7)	32	32	0	0	0
O2*	35(5)	35	35	0	0	0
MgSiO₃						
	10.0	GPa	This study			
Mg	33(7)	41(7)	63(2)	5(3)	0	0
Si	19(5)	40(5)	31(2)	2(2)	7(2)	-1(2)
O1	35(13)	47(13)	28(4)	17(7)	0	0
O2	47(9)	30(9)	37(3)	-2(4)	-2(3)	2(3)

* Constrained as isotropic.

TABLE 4. Linear axial compressibilities (GPa^{-1}) for comparison with previous studies

β_a	β_b	β_c	References
0.00121(9)	0.00098(11)	0.00123(7)	This study
0.00141	0.00107	0.00157	Kudoh et al. (1987)
0.00131	0.00120	0.00156	Yaganeh-Haeri et al. (1990)
0.00130	0.00104	0.00124	Ross and Hazen (1990)

TABLE 5. Atomic distances (\AA) and bond angles ($^\circ$) for perovskite-type MgSiO₃

Pressure (GPa)	0.0001	7.8	10.0	15.0
Si-O1 ($\times 2$)	1.801(1)	1.7837(5)	1.7779(8)	1.771(3)
Si-O2 ($\times 2$)	1.795(3)	1.782(1)	1.776(2)	1.775(5)
Si-O2 ($\times 2$)	1.783(3)	1.761(2)	1.763(2)	1.757(5)
Mg-O1	2.021(5)	1.995(2)	1.993(3)	1.995(10)
Mg-O1	2.092(4)	2.062(3)	2.062(3)	2.077(6)
Mg-O2 ($\times 2$)	2.055(3)	2.033(2)	2.022(2)	2.008(5)
Mg-O2 ($\times 2$)	2.285(3)	2.248(2)	2.247(2)	2.227(6)
Mg-O2 ($\times 2$)	2.424(3)	2.398(2)	2.391(2)	2.388(5)
av<Mg-O>viii	2.205(1)	2.177(1)	2.172(1)	2.165(2)
Mg-O1	2.844(5)	2.817(2)	2.808(3)	2.778(10)
Mg-O1	2.966(4)	2.951(3)	2.942(3)	2.939(6)
Mg-O2 ($\times 2$)	3.116(3)	3.099(2)	3.097(2)	3.104(5)
av<Mg-O>xii	2.474(1)	2.448(1)	2.443(1)	2.437(2)
Si-O1-Si	146.7(2)	146.1(1)	146.3(2)	146.2(6)
Si-O2-Si	147.3(2)	146.85(9)	146.6(1)	146.2(6)

TABLE 6. Cell volume- V_{SiO_6} - V_{MgO_8} tolerance factor (t_{MgO_8} and $t_{\text{MgO}_{12}}$) and bond length distortion factors (Δ_{SiO_6})

Pressure (GPa)	Cell volume- V_{SiO_6} - V_{MgO_8} (\AA^3)	t_{MgO_8}	$t_{\text{MgO}_{12}}$	Δ_{SiO_6}
0.0001	61.4(8)	0.870(3)	0.975(4)	1.0005(7)
7.8	59.4(6)	0.870(1)	0.974(1)	1.0005(6)
10.0	59.1(8)	0.867(1)	0.975(1)	1.0005(9)
15.0	58.6(4)	0.866(2)	0.975(2)	1.0003(26)

mean square relative displacements for Ca-O bonds in CaTiO₃ and CaGeO₃ perovskites are considerably larger than those for Ti-Ti and Ge-Ge frameworks.

Figure 2a shows the thermal ellipsoids calculated from anisotropic displacement parameters at ambient pressure. Thermal vibration of Mg atom is significantly anisotropic. The Mg site is considered to be in eightfold coordination, and a MgO₈ polyhedron shares one face and four edges with surrounding SiO₆ octahedra. Mean square displacements for Mg atoms are small in the direction perpendicular to the shared face and shared edges. The nearest Mg-O distance is two Mg-O1 (2.021 \AA), where Mg and O1 are located on a mirror plane. The thermal vibrations of Mg atoms are also restricted in the direction perpendicular to O1-O1 direction on the mirror plane.

We were able to refine anisotropic displacement parameters for all atoms in MgSiO₃ perovskite at 10 GPa. At higher pres-

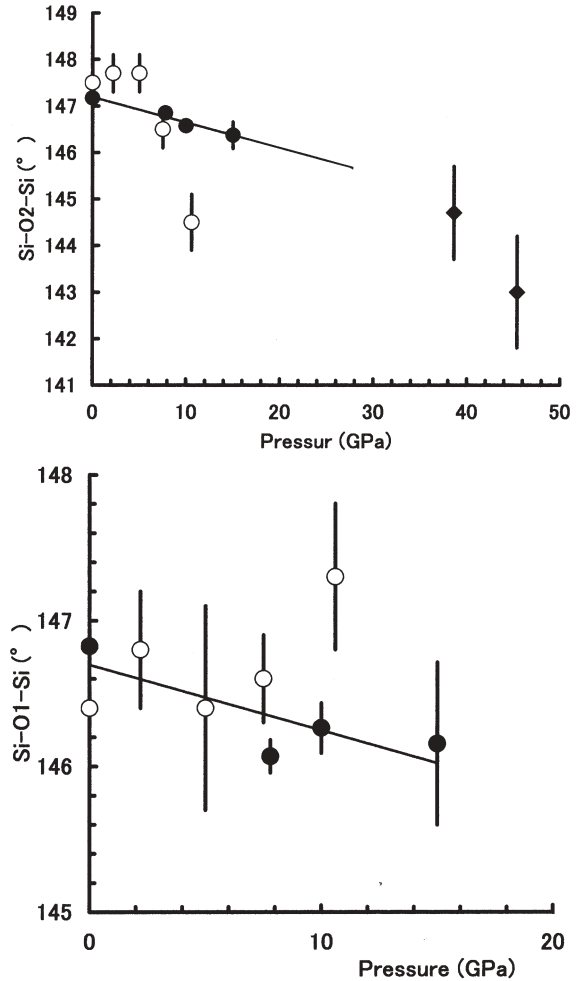


FIGURE 1. Variation of measured SiO₆ octahedral tilt angles in the a - b plane given by Si-O2-Si (upper figure) and SiO₆ octahedral tilt angles in the b - c plane given by Si-O1-Si (lower figure) for MgSiO₃ perovskite as a function of pressure. Open circles and open squares are from Ross and Hazen (1990), and solid circles and solid squares are from this study. Solid diamonds are from Fiquet et al. (2000). The increase of the orthorhombic distortion with increasing pressure, i.e., the decrease of the Si-O-Si angle, is obviously observed.

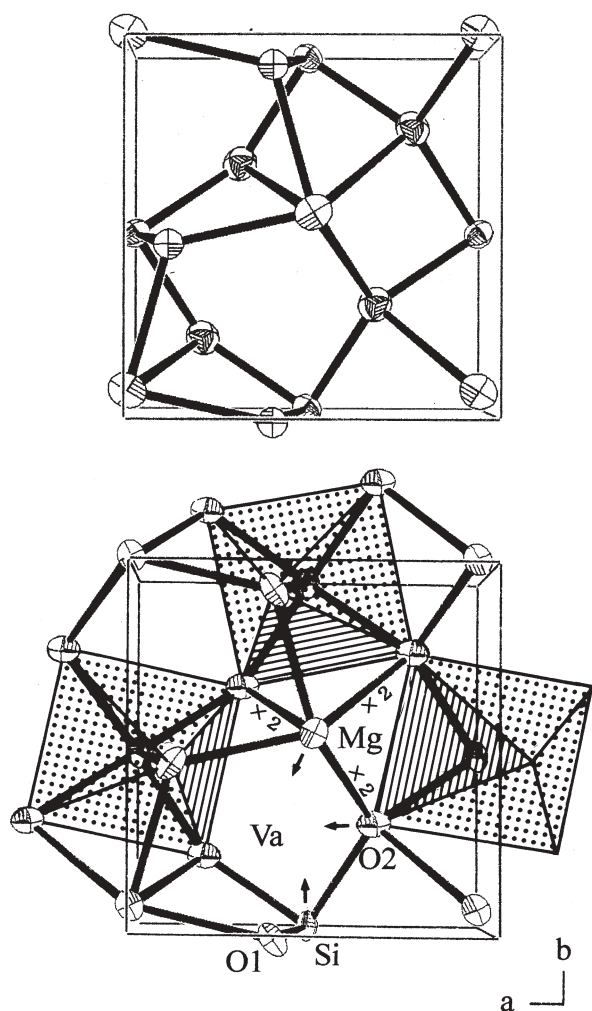


FIGURE 2. Perspective views of the structure of MgSiO₃ perovskite at 0.1 MPa (a) and 10 GPa (b). Displacement ellipsoids are drawn at the 99% probability. SiO₆ octahedra are indicated by shading. Va shows a vacant space in the structure.

sure, U_{11} and U_{22} of the Mg atom and U_{11} of the Si atom (Table 4) reduced significantly. The anisotropy of Mg atom at ambient pressure is also maintained under high pressure; its thermal vibrations are restricted toward the shared face, shared edges and shortest Mg-O1 directions. Moreover, a component of thermal vibration toward the vacant space is added when pressure is raised (Fig. 2b). Although MgSiO₃ perovskite has a dense structure and the average O-O distance is short (2.55 Å at 10 GPa), all distances in the structure become even shorter under

pressure. At high pressure, all the atoms have obvious anisotropy of thermal vibration. The largest amplitudes of thermal vibration for Mg, Si, and O2 atoms are directed toward vacant space in the structure (arrows in Fig. 2b). It seems that the thermal motion of O1 correlates with that of Mg on the same mirror plane and its larger amplitudes are in the direction parallel to tilting of SiO₆ octahedra. The behavior of atomic thermal motions in MgSiO₃ perovskite varies with pressure along with the structural variations, which indicates that the adiabatic effective potential depends on pressure.

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