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# High-pressure structural study of phase-A, $\text{Mg}_7\text{Si}_2\text{H}_6\text{O}_{14}$ using synchrotron radiation

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## Abstract

The specimen used in this study was a single crystal of phase-A  $\text{Mg}_{6.99}\text{Si}_{1.99}\text{H}_{6.06}\text{O}_{14}$  synthesized using a multi-anvil apparatus at conditions of 1000 °C and 10 GPa. Sets of x-ray diffraction intensities were measured with a single crystal of  $60 \times 50 \times 30 \mu\text{m}$  using synchrotron radiation up to 9.4 GPa. The unit-cell parameters observed gave  $K_0 = 105$  GPa (assuming that  $K' = 4$ ). With increasing pressure, significant decreases of O–O distances for hydrogen bonds were observed.

## 1. Introduction

In the investigation of the system  $\text{Mg}_2\text{SiO}_4\text{--MgO--H}_2\text{O}$  up to 18 GPa, Ringwood and Major [1] found three new hydrous phases, which they named phases A, B and C. Yamamoto and Akimoto [2] studied phase relations in the system  $\text{MgO--SiO}_2\text{--H}_2\text{O}$  up to 8 GPa and determined the chemical formula of phase A to be  $2\text{Mg}_2\text{SiO}_4 \cdot 3\text{Mg}(\text{OH})_2$ .

From the synthesis experiments on various bulk compositions in the system  $\text{MgO--SiO}_2\text{--H}_2\text{O}$ , Yamamoto and Akimoto [3] found that the phase was stable up to the highest pressure of the experiments, 7.7 GPa. Kanzaki [4] investigated the stability of phase A and observed that phase A was stable up to 15 GPa at below 1000 °C. The crystal structure of phase A was determined and well established at ambient pressure from a single-crystal x-ray diffraction study by Horiuchi *et al* [5]. Pawley *et al* [6] studied thermal expansivity and compressibility of phase A and reported  $K_0 = 145$  GPa ( $K' = 4$ ) from powder x-ray diffraction. Luth [7] raised the question of whether phase A is relevant to the Earth's mantle. Pawley and Wood [8] reported a positive slope in the  $P\text{--}T$  diagram for the boundary of phase A  $\leftrightarrow$  forsterite+brucite in contrast to the negative  $P\text{--}T$  slope of Yamamoto and Akimoto [3]. Kagi *et al* [9] reported that

**Table 1.** Unit-cell parameters, number of  $I_0$ , and  $R$ -values.

$P$ (GPa)	0 <sup>a</sup>	0	4.5	9.1	9.4
$a$ (Å)	7.8603(2)	7.8604(7)	7.756(1)	7.6445(3)	7.644(1)
$c$ (Å)	9.5730(2)	9.5702(8)	9.469(3)	9.383(7)	9.371(2)
$2\theta_{max}$ (deg)	107.9	60.0	90.0	60.0	80.0
Radiation	Mo $K\alpha$	Mo $K\alpha$	Synchrotron		
No of $I_0$	379	363	299	164	255
	$I_0 \geq 1.5\sigma I_0$	$I_0 \geq 3\sigma I_0$	$I_0 \geq 3\sigma I_0$	$I_0 \geq 1.5\sigma I_0$	$I_0 \geq 3\sigma I_0$
$R$ (%)	5.9	5.0	9.6	7.4	7.9
$R_w$ (%)		6.0	9.1	8.4	7.3

<sup>a</sup> Data from [5].

H atoms occupy two distinct sites and that increased pressure further increases the hydrogen bonding of D1 compared to D2, from the results of neutron powder diffraction at ambient pressure and 3.2 GPa and IR and NMR spectra.

These studies indicate that phase A is a possible H<sub>2</sub>O-bearing mineral phase in the subduction zone in the Earth's mantle at least down to 400 km.

In this study we conducted the structural analysis of phase A at high pressures up to 9.4 GPa with a single-crystal x-ray diffraction method using a diamond anvil cell and synchrotron radiation in order to investigate the effect of pressure on the crystal structure, especially on the local environment surrounding the hydrogen atoms.

## 2. Experimental details

The specimen used in this study was a single crystal of phase-A Mg<sub>7</sub>Si<sub>2</sub>H<sub>6</sub>O<sub>14</sub> synthesized by Kagi *et al* [9] using a multi-anvil apparatus at conditions of 1000 °C and 10 GPa. Results of electron microprobe analysis yield a chemical composition of Mg<sub>6.99</sub>Si<sub>1.99</sub>H<sub>6.06</sub>O<sub>14</sub>. The difference in the total weight was ascribed to H<sub>2</sub>O.

Sets of x-ray diffraction intensities up to  $\sin \theta/\lambda = 0.7\text{--}1.0 \text{ \AA}^{-1}$  were measured with a single crystal of  $60 \times 50 \times 30 \mu\text{m}$  using synchrotron radiation of wavelengths 0.6965, 0.6993 and 0.7026 Å at 4.5, 9.1 and 9.4 GPa, respectively at the beamline BL-10A, Photon Factory, Tsukuba, Japan. The modified Merrill–Bassett-type diamond anvil pressure cell [10] was used. A 0.25 mm thick stainless steel (SUS301) plate was used as gasket material. As a fluid pressure medium, a 4:1 mixture of methanol and ethanol was used. The pressure was calibrated using the ruby fluorescence method.

The unit-cell parameters obtained using 15–24 reflections with  $2\theta$  from 10° to 50° are given in table 1. Out of 2300 reflections in a sphere which were accessible with the diamond anvil high-pressure cell, a total of 164–299 symmetry-independent reflections ( $I_0 \geq 1.5\sigma I_0$  to  $I_0 \geq 3\sigma I_0$ ) were obtained by averaging the symmetry-equivalent intensities in Laue group  $6/m$ . Intensities were corrected for the Lorentz factor and no absorption correction was applied because of the sufficiently small value of  $\mu r$  ( $<0.04$ ).

## 3. Results and discussion

The mode of data collections and final agreement factors applying the weight  $1/\sigma_{hkl}^2$  for each reflection are given in table 1. The final atomic parameters with the space group  $P6_3$  (No 173) are given in table 2. The unit-cell parameters and atomic parameters at ambient pressure agree well with those of Horiuchi *et al* [5]. The unit-cell parameters in table 1 gave  $K_0 = 105$  GPa

**Table 2.** Atomic parameters.

<i>P</i> (GPa)		0 <sup>a</sup>	0	4.5	9.1	9.4
Si1	<i>z</i>	0.1741(4)	0.1763(6)	0.1785(23)	0.1911(20)	0.1829(22)
	<i>B</i>	0.33(1)	0.47(9)	0.40(9)	0.6(1)	0.0(1)
Si2	<i>z</i>	0.4018(4)	0.4080(11)	0.4079(24)	0.4070(24)	0.4092(24)
	<i>B</i>	0.36(1)	0.47(7)	0.26(8)	0.3(1)	0.6(1)
Mg1	<i>x</i>	0.3722(1)	0.3721(4)	0.3734(6)	0.3752(6)	0.3757(6)
	<i>y</i>	0.4547(1)	0.4548(4)	0.4584(7)	0.4583(7)	0.4602(6)
	<i>z</i>	0.3857(4)	0.3888(6)	0.3878(21)	0.3946(15)	0.3901(21)
	<i>B</i>	0.56(1)	0.57(5)	0.47(6)	0.7(1)	0.5(1)
Mg2	<i>x</i>	0.2252(1)	0.2236(4)	0.2215(6)	0.2192(6)	0.2206(6)
	<i>y</i>	0.2438(1)	0.2438(4)	0.2434(7)	0.2443(6)	0.2450(6)
	<i>z</i>	0.1127(4)	0.1144(5)	0.1179(20)	0.1257(16)	0.1224(20)
	<i>B</i>	0.49(1)	0.45(5)	0.33(6)	0.2(1)	0.5(1)
Mg3	<i>z</i>	0.1029(4)	0.1061(7)	0.1101(26)	0.1208(21)	0.1130(25)
	<i>B</i>	0.50(2)	0.31(10)	0.9(1)	0.0(1)	0.9(1)
O1	<i>x</i>	0.2001(3)	0.2040(8)	0.2077(11)	0.2011(13)	0.2097(11)
	<i>y</i>	0.0274(3)	0.0294(8)	0.0317(13)	0.0302(14)	0.0330(13)
	<i>z</i>	−0.0240(4)	−0.0219(8)	−0.0230(24)	−0.0269(32)	−0.0229(24)
	<i>B</i>	0.46(2)	0.26(9)	0.0(1)	0.9(2)	0.0(1)
O2	<i>x</i>	0.4766(3)	0.4759(8)	0.4728(15)	0.4748(13)	0.4700(12)
	<i>y</i>	0.0988(3)	0.0983(8)	0.0985(15)	0.1046(13)	0.0985(12)
	<i>z</i>	0.4844(4)	0.4853(8)	0.4848(20)	0.4836(22)	0.4815(20)
	<i>B</i>	0.51(2)	0.17(8)	0.4(1)	0.0(2)	0.0(1)
O3	<i>x</i>	0.4538(3)	0.4510(7)	0.4500(11)	0.4475(10)	0.4486(10)
	<i>y</i>	0.2947(3)	0.2927(7)	0.2891(11)	0.2827(10)	0.2873(11)
	<i>z</i>	0.2320(4)	0.2334(8)	0.2421(29)	0.2472(24)	0.2517(30)
	<i>B</i>	0.54(2)	0.13(9)	0.0(1)	0.0(2)	0.5(1)
O4	<i>x</i>	0.1704(3)	0.1660(7)	0.1634(10)	0.1539(11)	0.1604(9)
	<i>y</i>	0.4367(3)	0.4344(7)	0.4344(11)	0.4310(11)	0.4370(10)
	<i>z</i>	0.2398(5)	0.2406(8)	0.2443(27)	0.2628(29)	0.2549(25)
	<i>B</i>	0.54(2)	0.24(9)	0.0(1)	0.0(2)	0.0(1)
O5	<i>B</i>	0.53(3)	0.21(14)	0.0(2)	0.9(4)	0.0(2)
O6	<i>z</i>	0.2323(6)	0.2359(12)	0.2341(32)	0.2405(33)	0.2401(33)
	<i>B</i>	0.52(3)	0.15(14)	0.0(2)	0.0(2)	0.0(2)

<sup>a</sup> Data from [5]. *z* for O5 was fixed at 0.0 as the origin.

(assuming that  $K' = 4$ ) with the third-order Birch–Murnaghan equation of state. The single-crystal x-ray data from the present work do not agree with the  $K_0 = 145$  GPa (assuming that  $K' = 4$ ) value obtained from powder x-ray data of Pawley *et al* [6]. The difference is presumed to be due to a difference in hydrostaticity.

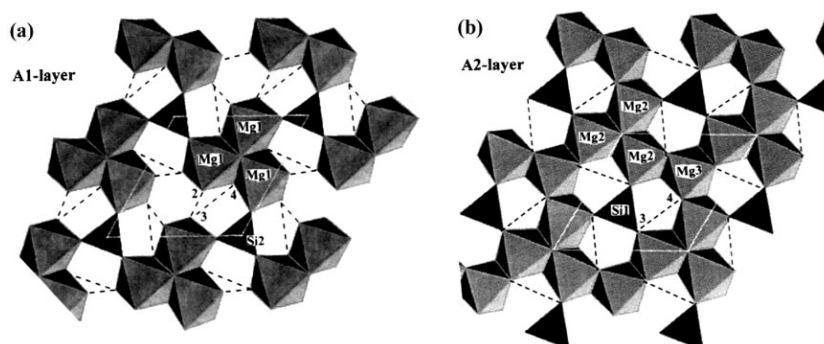
As shown in table 3, marked compression was observed in the Mg1 octahedron. The mean Mg–O distance of the Mg1O<sub>6</sub> octahedron decreased by around 5% at 9.4 GPa, while those of Mg2O<sub>6</sub> and Mg3O<sub>6</sub> octahedra remained almost constant. The mean Si–O distance of the Si2O<sub>4</sub> tetrahedron decreased by around 2% at 9.4 GPa, while that of the Si1O<sub>4</sub> tetrahedron remained almost constant.

O2 and O4 are most probably hydroxyl ions because O2 and O4 are coordinated by only Mg atoms with total charges of +1 and +1.33, respectively [5].

As pointed out by Horiuchi *et al* [5], the crystal structure of phase A is based on the ABCB closest packing of O<sup>2−</sup> and OH<sup>−</sup>. The structure consists of two types of layer, A1 and A2, which are stacked alternately along the direction of the *c*-axis. The A1 layer is made

**Table 3.** Interatomic distances (Å).

<i>P</i> (GPa)	0 <sup>a</sup>	0	4.5	9.1	9.4
Si1–O3 [3]	1.641(3)	1.653(5)	1.65(1)	1.61(1)	1.65(1)
–O5	1.666(4)	1.69(1)	1.69(3)	1.79(2)	1.71(3)
Mean	1.647(3)	1.662(6)	1.66(2)	1.66(1)	1.67(2)
Si2–O1 [3]	1.639(3)	1.660(6)	1.64(1)	1.56(2)	1.62(1)
–O6	1.623(7)	1.63(1)	1.65(4)	1.56(4)	1.58(4)
Mean	1.635(4)	1.653(7)	1.64(2)	1.56(3)	1.61(2)
Mg1–O1	2.018(3)	1.992(6)	1.96(1)	1.94(2)	1.93(1)
–O2	1.996(4)	1.987(6)	1.98(2)	1.94(2)	1.93(1)
–O3	2.229(4)	2.239(6)	2.18(2)	2.18(2)	2.12(2)
–O4	2.065(4)	2.099(6)	2.06(2)	2.02(2)	2.01(2)
–O4′	2.329(4)	2.398(6)	2.31(2)	2.20(2)	2.20(2)
–O5	2.139(2)	2.123(6)	2.08(2)	2.03(1)	2.04(1)
Mean	2.140(4)	2.140(6)	2.10(2)	2.05(2)	2.04(2)
Mg2–O1	2.076(4)	2.075(6)	2.08(2)	2.13(3)	2.09(2)
–O1′	2.204(4)	2.207(6)	2.21(2)	2.22(3)	2.21(2)
–O2	2.025(2)	2.028(6)	2.01(2)	2.04(2)	2.01(2)
–O3	1.993(4)	1.988(7)	2.01(2)	1.98(2)	2.01(2)
–O4	2.149(4)	2.141(6)	2.12(2)	2.16(2)	2.14(1)
–O6	2.173(3)	2.168(6)	2.12(2)	2.08(2)	2.10(2)
Mean	2.103(4)	2.101(6)	2.09(2)	2.10(2)	2.09(2)
Mg3–O2 [3]	2.040(4)	2.057(6)	2.06(2)	2.07(2)	2.07(2)
–O4 [3]	2.076(4)	2.078(5)	2.05(2)	2.11(3)	2.07(2)
Mean	2.058(3)	2.068(6)	2.06(2)	2.09(3)	2.07(2)

<sup>a</sup> Data from [5].**Figure 1.** The A1 layer (a) and A2 layer (b) of phase A. O2–O3 and O4–O3 are indicated by broken lines.

up of Si<sub>2</sub>O<sub>4</sub> tetrahedra and Mg<sub>1</sub>O<sub>6</sub> octahedra. The A2 layer is made up of SiO<sub>4</sub> tetrahedra and Mg<sub>2</sub>O<sub>6</sub>. The arrangement of SiO<sub>4</sub> tetrahedra and MgO<sub>6</sub> octahedra of the A1 layer is identical to that of the A2 layer except for additional Mg<sub>3</sub>O<sub>6</sub> octahedra (figure 1).

In the A1 layer, the Mg<sub>3</sub>O<sub>6</sub> octahedron of the A2 layer is replaced by the hydrogen atoms which locate around the threefold symmetry axis. These hydrogen atoms form hydrogen bonds in O2–H1···O3 and O4–H2···O3 as pointed out by Kagi *et al* [9].

From the study of neutron powder diffraction data for phase A at ambient pressure and 3.2 GPa, Kagi *et al* [9] reported that increased pressure further increases the hydrogen bonding

**Table 4.** O–O distances (Å) around H.

<i>P</i> (GPa)	0 <sup>a</sup>	0	4.5	9.1	9.4
O2–O3	2.918(5)	2.91(1)	2.79(3)	2.66(3)	2.64(2)
O4–O3	3.187(4)	3.168(9)	3.06(2)	2.92(1)	2.99(1)

<sup>a</sup> Data from [5].

of D1 compared to D2 and that O4–D2···O3 showed no significant increase or decrease in hydrogen bonding in the pressure range investigated. Our results in the present study are in general agreement with the observation of Kagi *et al* [9]. The O–O distances around hydrogen atoms in table 4 indicate that both O2–O3 and O4–O3 distances significantly decrease and O2–O3 distances decrease more than O4–O3 distances with increasing pressure. O2–O3 distances decrease by around 10% at 9.4 GPa, while O4–O3 distances decrease by around 6% at the same pressure. It should be noted that the trend of O4–O3 is in line with the O–O decrease in brucite up to 9.3 GPa reported by Parise *et al* [11].

The marked compression of the Mg<sub>1</sub>O<sub>6</sub> octahedron and Si<sub>2</sub>O<sub>4</sub> tetrahedron observed in this study can be interpreted in terms of the compression of the hydrogen bonds adjacent to the Mg<sub>1</sub>O<sub>6</sub> octahedron and the Si<sub>2</sub>O<sub>4</sub> tetrahedron.

The decrease in O–O distances for hydrogen bonds with pressure observed in this study suggests that the upper thermal stability limit of phase A might be extended by applying pressure. This is consistent to the result of a positive slope in the *P–T* diagram for the boundary of phase A ↔ forsterite + brucite observed in the equilibrium experiments by Pawley and Wood [8].

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