In-situ high pressure X-ray diffraction of phase E to 15 GPa

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ABSTRACT

In-situ high pressure X-ray diffraction of phase E (free of secondary phases) measured up to 14.5 GPa shows that phase E is stable over this pressure range at room temperature. The pressure dependence of the lattice parameters are \( a = 2.967 - 0.011P + 0.0001P^2 \) and \( c = 13.886 - 0.054P + 0.001P^2 \) (\( P \) is in GPa). A least-squares fit to third-order of Eulerian strain theory yields a bulk modulus \( K_0 \) for phase E of 93 (±4) GPa and pressure derivative \( K'_0 \) of 5 (±1). The bulk modulus obtained by this study is about 10% lower than that obtained by Brillouin scattering. Phase E appears to have the lowest bulk modulus among DMHS. The OH stretching frequency of 3613 cm\(^{-1}\) indicates weak, if any, hydrogen bonding. The associated O-O distance of phase E is estimated to be 3.00–3.10 Å.

INTRODUCTION

Phase E belongs to the family of dense hydrous magnesium silicates (DHMS) that can form by the reaction of \( \text{H}_2\text{O} \) with nominally anhydrous minerals (NAMs) thought to be present in the Earth’s mantle. A number of experimental studies have established the \( P-T \) stability fields of DHMS (Ringwood and Major 1967; Liu 1987; Kanzaki 1991; Gasparik 1993; Irifune et al. 1998; Frost and Fei 1998; Shieh et al. 1998) confirming their potential role in transporting water into the transition zone, and possibly into the lower mantle as well. The introduction of \( \text{H}_2\text{O} \) into the deep mantle, residing in DHMS or via partitioning between DHMS and NAMs, has far reaching consequences for the rheology (Karato 1986; Hirt and Kohlstedt 1996), electrical conductivity (Karato 1990), and melting relations (Karato et al. 1986; Hirt and Kohlstedt 1996),ing between DHMS and NAMs, has far reaching consequences for the rheology (Karato 1986; Hirt and Kohlstedt 1996), electrical conductivity (Karato 1990), and melting relations (Karato et al. 1986; Hirt and Kohlstedt 1996), whether the unusual long-range disorder is an intrinsic feature of the present in-situ X-ray diffraction to study the behavior of phase E at high pressure. In particular, we address the question whether the unusual long-range disorder is an intrinsic feature of the phase E structure at high pressure or a result of quench modification.

EXPERIMENTAL METHOD

Phase E was synthesized at 14.5 GPa and 1000 °C in a Walker-type multi anvil press using a 2:1 mixture of brucite and \( \text{SiO}_2 \) as starting material (Kanzaki 1991). The composition of phase E was analyzed with the electron microprobe (JEOL Superprobe) using pure synthetic \( \text{MgO} \) and \( \text{SiO}_2 \) as standards and a beam current of 5 nA with a rastered beam of 20 µm in order to minimize beam damage. Assuming the deficit in analytical totals to be \( \text{H}_2\text{O} \), the average composition (n = 12) of phase E is 38.1(3) wt% \( \text{SiO}_2 \), 48.4(3) wt% \( \text{MgO} \), and 13.6(3) wt% \( \text{H}_2\text{O} \), which is equivalent to \( \text{Mg}_2\text{Si}_{1.18}\text{H}_2\text{O}_6 \) when normalized to 6 O atoms (Kanzaki 1991) and the Mg/Si ratio is about 1.89. Raman spectra were recorded from unoriented crystals of phase E using \( \text{Ar}^+ \) 488 nm with 30 mW power and 1000 second collecting times. The spectrum shows peaks at 242, 444, 684, 864, 937, and 1507 cm\(^{-1}\) with a single broad peak in the

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OH-stretching region at 3613 cm⁻¹, which is in good agreement with results obtained by Frost and Fei (1998), but differs from the results obtained by Liu et al. (1997).

For high-pressure experiments, the sample was ground into powder and loaded into a gasketed (T301 stainless steel with a 200 μm hole) modified Merrill-Bassett type diamond anvil cell. Two different runs were designed in this experiment. In one run, the sample was loaded with ruby chips (5–10 μm), and an ethanol-methanol mixture (4:1) was used as pressure medium. In the other run, the sample was placed together with a tiny Au foil and ruby chips (5–10 μm), and loaded with helium gas as pressure medium. The pressure was obtained by the ruby fluorescence method (Mao et al. 1978) and the equation of state of Au (Jamieson et al. 1982).

High-pressure energy dispersive X-ray diffraction experiments were carried out at beamline X17C National Synchrotron Light Source, Brookhaven National Laboratory. The synchrotron radiation was operating produced from electron storage ring energies and currents of 2.8 GeV and 300–160 mA and data were collected with a solid state Ge detector cooled by liquid nitrogen with a fixed 2Θ = 12° or 9°. The samples were first examined by X-ray diffraction at ambient pressure with results obtained by Frost and Fei (1998), but differs from a different Mg/Si ratio and H₂O content (these were not described above, phase E has a nonstoichiometric nature, variation of bulk modulus may result from a different Mg/Si ratio and H₂O content (these were not reported by Bass et al. for their sample).

RESULTS

Phase E was found to be stable at pressures to 14.5 GPa and no phase transition was observed (Fig. 1). Effects of pressure on the unit-cell parameters and volumes of phase E in two different runs are tabulated in Table 1. The starting material has unit-cell parameters of \( a = 2.9701 \) Å, \( c = 13.882 \) Å, and \( V = 106.05 \) Å³; all are lower than those reported by Kudoh et al. (1993) \( (a = 2.9853 \) Å, \( c = 13.9482 \) Å, \( V = 107.65 \) Å³), and our density is higher (\( \rho = 2.92 \) g/cm³ as compared to \( \rho = 2.78 \) and 2.88 g/cm³). The unit-cell parameters as a function of pressure are plotted in Figure 2. The pressure dependences of the a axis can be represented by \( a = 2.967 - 0.011P + 0.0002P² \) and the c axis by \( c = 13.886 - 0.054P + 0.001P² \), where P is the pressure in GPa. The lattice parameters of phase E have a nonlinear dependence on pressure over this range. The c axis is more compressible than the a axis such that the \( c/a \) ratio increases only slightly with pressure increase (Fig. 3). The linear compressibilities of a and c axes (at ambient conditions) are \( \beta_a = 4.23 \times 10^{-2} \) GPa⁻¹ and \( \beta_c = 5.14 \times 10^{-2} \) GPa⁻¹. The equation of state data of phase E were evaluated by least squares fits of the normalized pressure \( f \) Eulerian strain (f) (Birch 1978). The Eulerian strain is given by:

\[
f = \frac{1}{2} \left( \frac{V_0}{V} \right)^{2/3} - 1 \tag{1}
\]

where \( V \) is the volume and \( V_0 \) is the ambient pressure volume. The normalized pressure is

\[
P = \frac{f}{3f(1+2f)^{5/2}} \tag{2}
\]

where \( P \) is the measured pressure. The Birch-Murnaghan equation fit to third order in the strain energy is:

\[
F = K_T \left[ 1 + \frac{3}{2} \left( \frac{K_T}{2} - 4f \right) \right] \tag{3}
\]

where \( K_T \) is the bulk modulus and \( K_T \) is the pressure derivative at room temperature. Figure 4 plots \( F \) against \( f \).

A least-squares analysis of the weighted data yields a bulk modulus of 93 (±4) GPa and pressure derivative of 5 (±1). By comparison, a fit to a second-order Birch-Murnaghan equation of state (\( K_T \) set equal to 4) yields \( K_T = 94 \) (±2) GPa. The unit-cell volume data as a function of pressure are plotted in Figure 5.

Bass et al. (1991) reported a bulk modulus of Phase E by Brillouin scattering that is 60% lower than that of \( \beta\)-Mg₂SiO₄; using the bulk modulus of \( \beta\)-Mg₂SiO₄ of 170 GPa (Zha et al. 1997), this corresponds to a bulk modulus ~102 GPa which is about 10% higher than the value obtained in this study. As described above, phase E has a nonstoichiometric nature, variable density, and chemical composition. Therefore the discrepancy in the measurement of bulk modulus may result from a different Mg/Si ratio and H₂O content (these were not reported by Bass et al. for their sample).

**TABLE 1.** Lattice parameter of phase E under pressure at ambient temperature

<table>
<thead>
<tr>
<th>Run</th>
<th>( P ) (GPa)</th>
<th>( a ) (Å)</th>
<th>( c ) (Å)</th>
<th>( V ) (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.0001</td>
<td>2.9653(5)</td>
<td>13.890(4)</td>
<td>105.77(4)</td>
</tr>
<tr>
<td>A2</td>
<td>1.0(1)</td>
<td>2.9580(7)</td>
<td>13.827(4)</td>
<td>104.77(5)</td>
</tr>
<tr>
<td>A3</td>
<td>2.7(1)</td>
<td>2.9416(26)</td>
<td>13.758(16)</td>
<td>103.10(17)</td>
</tr>
<tr>
<td>A4</td>
<td>3.6(2)</td>
<td>2.9303(9)</td>
<td>13.704(7)</td>
<td>101.91(6)</td>
</tr>
<tr>
<td>B1</td>
<td>1.4(1)</td>
<td>2.9513(14)</td>
<td>13.806(10)</td>
<td>104.14(9)</td>
</tr>
<tr>
<td>B2</td>
<td>6.5(2)</td>
<td>2.9060(11)</td>
<td>13.626(10)</td>
<td>99.66(9)</td>
</tr>
<tr>
<td>B3</td>
<td>8.0(1)</td>
<td>2.8948(19)</td>
<td>13.531(11)</td>
<td>98.20(12)</td>
</tr>
<tr>
<td>B4</td>
<td>8.9(2)</td>
<td>2.8880(27)</td>
<td>13.512(16)</td>
<td>97.60(17)</td>
</tr>
<tr>
<td>B5</td>
<td>10.0(4)</td>
<td>2.8812(20)</td>
<td>13.485(12)</td>
<td>96.95(12)</td>
</tr>
<tr>
<td>B6</td>
<td>11.5(4)</td>
<td>2.8741(9)</td>
<td>13.447(5)</td>
<td>96.20(5)</td>
</tr>
<tr>
<td>B7</td>
<td>12.8(5)</td>
<td>2.8647(10)</td>
<td>13.414(6)</td>
<td>95.34(6)</td>
</tr>
<tr>
<td>B8</td>
<td>14.5(5)</td>
<td>2.8590(6)</td>
<td>13.409(4)</td>
<td>94.92(4)</td>
</tr>
</tbody>
</table>
DISCUSSION

Phase E maintains its disordered structure on room temperature compression to at least 14.5 GPa at room temperature without phase transitions or amorphization. We infer that the basic cation disordered structure of the phase is not a result of pressure quenching. Whether or not this disorder in phase E results from temperature quenching (e.g., the synthesis conditions) requires additional data from in-situ high P-T study. It should be noted, however, that after a run duration of six hours in the synthesis, phase E forms large (200–300 µm) isometric crystals, inconsistent with a quench origin. In such a case, phase E may act like a competitor for H₂O with hydrous wadsleyite (\(\beta\)-Mg₂SiO₄) at transition zone pressures, given sufficient H₂O. Phase E can contain up to \(\sim\)10 wt% H₂O, whereas hydrous wadsleyite holds only \(\sim\)3 wt% (Inoue et al. 1995). Kawamoto and Holloway (1997) suggested that phase E would be one of the dominant hydrous phase in the peridotite mantle at pressures near 11 GPa and temperatures below 1000 °C, whereas phase E may coexist with hydrous \(\beta\)-Mg₂SiO₄ at 13.5–16.5 GPa and 1200–1425 °C. In contrast, at 15.5 GPa hydrous \(\beta\)-Mg₂SiO₄ is the dominant phase at either low H₂O environments (e.g., 3.4 wt%) or temperatures above 1500 °C, i.e., near the mantle adiabat (Inoue 1994; Inoue et al. 1995; Kawamoto et al. 1996). The experimental data show that phase E exists at lower temperature in comparison with the stability field of hydrous wadsleyite (Inoue et al. 1995). As such, phase E could serve as a H₂O-host material in cooler regions such as within subducting slabs.

Phase E is nonstoichiometric and has a layer-type structure similar to phase D. However, the linear compressibilities of phase E are an order magnitude larger than those of phase D [phase D: \(\beta_{ao} = 1.56 \times 10^{-3}\) GPa⁻¹ and \(\beta_{co} = 3.18 \times 10^{-3}\) GPa⁻¹ (Frost and Fei 1998)]. The \(c/a\) ratio of phase E is essentially independent of pressure, whereas a negative slope is reported for phase D (Frost and Fei 1998). Anisotropic compression
commonly occurs in layered structures as a result of differential bond strength and direction within and between layers. However, the intra- and inter-layer structure of phase E behaves in an unusual way compared to those of other layered mineral phases, such as brucite (Duffy et al. 1995) and phase D (Yang et al. 1997; Frost and Fei 1999). A possible explanation may be sought in the characteristic features of the phase such as its missing cations in the brucite-like layer and a pattern of vacancies and interlayer cations that are only ordered locally (Kudoh et al. 1993).

With $\rho = 2.92$ g/cm$^3$ and $K_T = 93 \pm 4$ GPa, phase E has the lowest density and bulk modulus of the DHMS reported to date (Table 2 and Fig. 6). This is consistent with Si in phase E (and phase A) having tetrahedral coordination (Kudoh et al. 1993) compared to mixed fourfold/sixfold coordination in hydrous and superhydrous phase B (shyB), and exclusive sixfold coordination in phase D, the latter showing the highest density and bulk modulus of DHMS phases known to date (Frost and Fei 1998). The linear relationship in Figure 6 indicates a strong correlation between bulk modulus and density, which in turn correlates with higher coordination of Si (fourfold-coordination in phase A and E, fourfold and sixfold coordination in shyB and B, and sixfold coordination in D).

Finally, our data provide information on the behavior of the hydrogen in the structure of phase E, a subject of some uncertainty (Kudoh et al. 1993). Phase E has the largest OH stretching frequency for the main peaks among the DHMS group (Table 2). However, weak peaks in several DHMS occur near 3600 cm$^{-1}$ (Cynn et al. 1996). It is interesting to examine possible correlation between the OH stretching mode and either bulk modulus or density. Correlations between OH stretching mode frequencies and OH-O distance have been studied extensively in a wide range of materials (Nakamoto et al. 1955; Vos et al. 1996). The longer O-H-O distance is associated with a higher O-H stretching frequency; that is, a stronger OH covalent bond and weaker hydrogen bond. Using the correlation of hydrogen stretching frequency vs. bond distance for silicates (Nakamoto et al. 1955) gives an estimated O-O distance of 3.00–3.10 Å, indicating that the average distance of the linkage in phase E is longer than that of the other DHMS. This result implies that hydrogen bonding (if it formally exists in this material) is weak.

**ACKNOWLEDGMENTS**

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**FIGURE 5.** The effect of pressure on the volume of phase E. Solid line represents least-squares fit to a linear formulation of Eularian strain, dashed line represents data fitted to a second-ordered Birch-Murnaghan equation of state.

**FIGURE 6.** The relationship between bulk modulus and density for DHMS phases. The solid line represents the linear least squares fit to all the data. A = phase A, B = phase B, shyB = superhydrous phase B, D = phase D, E = phase E.

**TABLE 2.** Bulk moduli, density, and OH stretching data of DHMS

<table>
<thead>
<tr>
<th>Phase</th>
<th>$K_0$*</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>OH stretch (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>97*</td>
<td>2.959†</td>
<td>3400, 3515‡</td>
</tr>
<tr>
<td>B</td>
<td>163*</td>
<td>3.368§</td>
<td>3356, 3414∥</td>
</tr>
<tr>
<td>shyB</td>
<td>145 (±15)#</td>
<td>3.327**</td>
<td>3362, 3419‡</td>
</tr>
<tr>
<td>D</td>
<td>166 (±3)††</td>
<td>3.50‡‡</td>
<td>2847§§</td>
</tr>
<tr>
<td>E</td>
<td>93 (±4)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

REFERENCES CITED


Horiiuchi, H., Morinoto, N., Yamamoto, K., and Akimoto, S. (1979) Crystal structure of 2Mg$_2$SiO$_4$·3Mg(OH)$_2$, a new high-pressure structure type. American Mineralogist, 64, 593–598.


