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Crystal structure of the dense hydrous magnesium silicate, phase D

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ABSTRACT

Liu (1986, 1987) reported the diffraction pattern of a hydrous magnesium silicate resulting from the breakdown of serpentine at 22 GPa and 1000 °C and named this material ‘‘phase D.’’ Since that time there have been several reports of the synthesis of phase D, but its confirmed composition and crystal structure have not yet been reported. We synthesized a new dense hydrous magnesium silicate at 20 GPa and 1200 °C and solved its crystal structure ($R_w = 0.015$ and $R = 0.014$). The single crystal has composition $Mg_{1.11}Si_{1.89}H_{2.22}O_6$ (ideal formula: $MgSi_2H_2O_6$), cell parameters $a = 4.7453(4)$, $c = 4.3450(5)$ Å, and $V = 84.74(2)$ Å^3, and space group $P\bar{3}1m$. The crystal structure is relatively simple with all the Si occupying octahedral sites in a layer similar to that of brucite, but with one of every three octahedra vacant. The MgO_6 octahedra are located above and below each vacant octahedral site. All O-H bonding occurs between SiO_6 octahedral layers. This is the only high-pressure hydrous magnesium silicate structure reported to date that contains all octahedrally coordinated Si. The calculated density of phase D ($d_{cal} = 3.50$ g/cm^3) is substantially greater than any other high-pressure hydrous magnesium silicate phase.

INTRODUCTION

Thirty years ago, Ringwood and Major (1967) published results of synthesis at high pressure of three phases in the system $MgO-SiO_2-H_2O$ that were designated by the letters A, B, and C. Since that time there has been substantial work on this system at high pressure, and the characteristics of these three phases have been relatively well determined. However, in pursuing similar work, other investigators identified additional phases in the system and reported two different compositions labeled as D (Yamamoto and Akimoto 1977; Liu 1986), and others as E (Kanzaki 1989, 1991) , F (Kudoh et al. 1995), and G (Ohtani et al. 1997). Substantial confusion exists about the nature of phase D, not only because of the absence of compositional data, but also because the original X-ray diffraction pattern reported by Liu (1987) contained so few diffraction lines (and probably some from more than one phase) that attempts to index the pattern were not successful. It is our opinion that phase G has the same crystal structure and X-ray diffraction pattern as phase D. This paper describes the crystal structure of phase D.

EXPERIMENTAL METHOD

The phase D sample used in this study was synthesized at 20 GPa and 1200 °C with an experiment duration of 20 min in a multi-anvil apparatus. Microprobe analysis shows that the chemical composition of phase D varies considerably from crystal to crystal with the weight percent of H_2O ranging from 10 to 18% and Mg/Si from 0.56 to 0.70. The average composition based on six O atoms per formula is $Mg_{1.11}Si_{1.89}H_{2.22}O_6$. A single-crystal fragment (0.08 × 0.05 × 0.05 mm) was extracted from a polished mount of the sample that had been analyzed by electron microprobe. The crystal was chosen on the basis of optical examination and precession photography. The X-ray photographs showed that the crystal has trigonal symmetry. The crystal was placed on a Picker four-circle diffractometer equipped with an Mo X-ray tube (β-filtered). Unit-cell parameters, determined by fitting the positions of 14 reflections in the range $20° < 2\theta < 35°$ following the procedure of King and Finger (1979), are $a = 4.7453(4)$, $c = 4.3450(5)$ Å, and $V = 84.74(2)$ Å^3. These values are close to those determined by Ohtani et al. (1997) using synchrotron radiation: $a = 4.790(3)$, $c = 4.344(3)$ Å, and $V = 86.3(2)$ Å^3.

X-ray diffraction intensity data from a hemisphere of reciprocal space with $0° \leq 2\theta \leq 60°$ were collected using ω scans of 1° width in step increments of 0.025° and 3s per step counting time. Two standard reflections were checked every 5 h; no significant or systematic variations in intensities of the standard reflections were observed. Digitized step data were integrated by the method of Lehmann and Larsen (1974) with backgrounds manually reset when necessary. Corrections were made for Lorentz and polarization effects and for X-ray absorption by the crystal ($\mu = 11.05$ cm^{-1}). The total number of measured reflections was 461. Examination of measured reflections indicated the possible space groups $P312$, $P31m$, and $P\bar{3}1m$. After symmetry-equivalent reflections were averaged in Laue group $\bar{3}m$ ($R_{merge} = 0.018$), there were 93

TABLE 1. Atomic positional and displacement parameters of phase D

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{iso}	Occupancy
Mg	0	0	0	0.0322(5)	β_{11}	0.0099(6)	$\beta_{11}/2$	0	0	1.70(6)	1.00
Si	⅔	⅓	½	0.0087(2)	β_{11}	0.064(3)	$\beta_{11}/2$	0	0	0.56(3)	$Si_{0.945}Mg_{0.055}$
O	0.6327(2)	0	0.2716(2)	0.0091(3)	0.0103(5)	0.0120(5)	$\beta_{22}/2$	−0.0002(3)	0	0.73(4)	1.00
H	0.536(13)	0	0.091(10)							0.9(9)	0.37

reflections with $I > 2\sigma_I$, where σ_I is the standard deviation determined from the counting statistics.

Because the E-value statistics showed that the crystal structure is probably centric, we began solution of the phase D structure based on space group $P\bar{3}1m$ using direct methods. The positions of Mg (0,0,0) and Si (⅔,⅓,½) were first located. After convergence of the refinement with these two atoms included, the resulting difference Fourier maps revealed the position of O. A refinement with anisotropic displacement parameters for all atoms (Mg, Si, and O) and variable occupancies for the Mg and Si sites yielded $R_w = 0.019$ and $R = 0.018$. The refined site occupancies showed that the Mg site is fully occupied by Mg, whereas the Si site contained ~10% Mg in addition to Si. Thus, in subsequent refinements, the Mg occupancy at the Si site was constrained to the microprobe analysis result (5.5%). The difference -Fourier maps were examined again at convergence of the refinement and a small positive peak was found near ½,0,0. However, such a position for H would require H being bonded symmetrically to two O atoms with an O-O distance of 2.68 Å, which is unlikely because the symmetrically bonded H has been found to occur only where the O-H-O distance is very short (~2.48 Å) (Snyder and Ibers 1962; Chevrier et al. 1993). Accordingly, three additional models (Models 2, 3, and 4) were considered. Model 2 assumes that the structure has the non-centric space group $P31m$; Mg and Si are at the sites with point symmetries $3m$ and 3, respectively, whereas there are two crystallographically distinct O sites (O1 and O2), both having point symmetry m. The H atom is also at a site with point symmetry m. In this model, H is closer to O1 and farther from O2. Yet, the structure refinement based on this model resulted in a significant increase (4–6 times) in standard deviations for all atomic positional and displacement parameters compared to those determined for Model 1. This model was thus disregarded. Model 3 assumes that both Mg and Si are at the sites as they are in Model 1, whereas O and H are at the same sites as in Model 2. The structure was refined in the non-centric space group $P31m$ while imposing a center of inversion between O1 and O2. The resultant R_w and R factors are 0.015 and 0.014, respectively, and the O1-H and O2-H distances are 0.91 and 1.77 Å. In this model, all O1-H bond vectors point along $+c$ when the structure is viewed along a. Model 4 is based on the centric space group $P\bar{3}1m$ by assuming that H is disordered between two partially occupied sites, both having point symmetry m. This model produces no difference from Model 3 in terms of the refinement statistics, but it seems to be consistent with the data from the Raman and infrared absorption spectra measurements because the O-H stretching band in phase D is relatively broad, indicating some kind of disorder of the H position (Lu and Hemley, personal communication). Hence, Model 4 was adopted for the final refinement. The number of H atoms in the structure was constrained to the total charge difference between O and (Mg + Si). A twin refinement was also performed; the results showed practically no twin component.

TABLE 2. Selected interatomic distances and angles in phase D

Distance (Å)		Angle (°)		Distance (Å)	
Mg-O × 6	2.1050(9)	$O\text{-}Mg\text{-}O^{i}$	91.63(3)	$O\text{-}O^{i}$	3.019(2)
		$O\text{-}Mg\text{-}O^{ii}$	88.37(2)	$O\text{-}O^{ii}$	2.934(1)
		$O\text{-}Mg\text{-}O^{iii}$	180.00	$O\text{-}O^{iii}$	4.210
Si-O × 6	1.8050(6)	$O\text{-}Si\text{-}O^{i}$	92.66(3)	$O\text{-}O^{i}$	2.611(1)
		$O\text{-}Si\text{-}O^{ii}$	94.08(4)	$O\text{-}O^{ii}$	2.642(1)
		$O\text{-}Si\text{-}O^{iii}$	81.27(3)	$O\text{-}O^{iii}$	2.351(1)
		$O\text{-}Si\text{-}O^{iv}$	171.12(4)	$O\text{-}O^{iv}$	3.599(1)
H-O	0.91(5)	$O\text{-}H\text{-}O^{iii}$	177.0(5)	$O\text{-}O^{iii}$	2.676(1)
$H\text{-}O^{iii}$	1.77(5)				
Mg-H	2.24(6)				
Si-Si	2.7395(2)				
Si-H	2.25(3)				
$H\text{-}H^{iii}$	0.86(9)				

Note: Symmetry code: i = $0,x,z$; ii = $0,-x,-z$; iii = $-x,0,-z$; iv = $x,x,-z$.

Least-squares refinements were performed using an updated version of RFINE4 (Finger and Prince 1975). Neutral atomic scattering factors, including anomalous dispersion corrections for Mg, Si, and O, were taken from *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974). Weighting schemes were based on $w = [\sigma^2(F) + (pF)^2]^{-1}$, where p is adjusted to ensure that the errors were normally distributed through probability plot analysis (Ibers and Hamilton 1974). Type II isotropic extinction corrections (Becker and Coppens 1975) were applied in the refinements. Final R_w and R factors are 0.015 and 0.014, respectively. Atomic positional coordinates and displacement parameters are presented in Table 1 and selected interatomic distances and angles in Table 2.

RESULTS AND DISCUSSION

The crystal structure of phase D is simply based on a hexagonal closest-packed array of O atoms. All cations except H are in octahedrally coordinated sites. One of the interesting features of the phase D structure is that the SiO_6 and MgO_6 octahedra occur in two separate layers stacked along c (Fig. 1). In the SiO_6 octahedral layer, each SiO_6 octahedron shares three edges with others to form

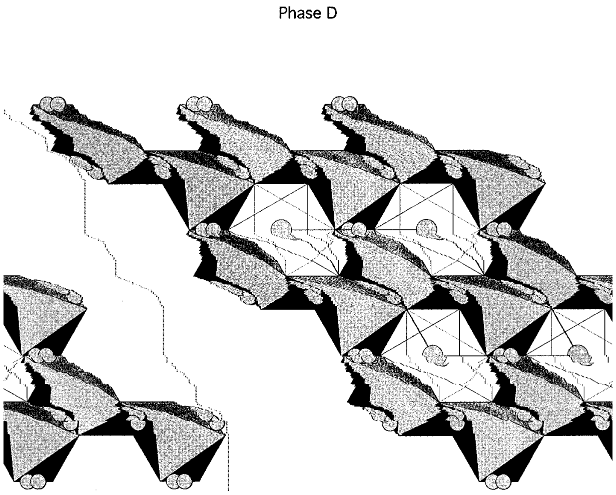

FIGURE 1. Crystal structure of phase D projected along *c*. Shaded and unshaded octahedra represent SiO_6 and MgO_6 octahedra, respectively. Large spheres represent Mg and small ones H.

TABLE 3. Powder diffraction data for phase D

			Liu (1987)		This study		Ohtani et al. (1997)	
h	*k*	*l*	*d*	*I*	*d*	*I*	*d*	*I*
			9.5	10				
0	0	1	4.3	15	4.345	23		
1	0	0			4.110	16		
			3.37	15				
1	0	1	3.00	100	2.986	100	3.00	s
			2.53	15				
1	1	0			2.373	10	2.38	vw
0	0	2			2.173	0		
1	1	1			2.082	82	2.09	s
2	−1	1						
2	0	0			2.055	5		
1	0	2			1.921	0		
2	0	1			1.858	26	1.87	m
1	1	2	1.61	80	1.602	76	1.61	s
2	−1	2						
2	1	0			1.553	0		
2	0	2			1.493	2	1.51	vvw
2	1	1	1.496	20	1.463	25	1.47	vw
3	−1	1						
0	0	3			1.448	0		
3	0	0	1.390	20	1.370	33	1.35	vvw

brucite-like layers with one of three octahedral sites vacant; these layers are interconnected by MgO_6 octahedral layers where two of three octahedra are vacant. The MgO_6 octahedra are located above and below each vacant octahedron in the SiO_6 octahedral layers. Another prominent feature of the structure is that the MgO_6 octahedron does not share edges with any other occupied polyhedra, which makes space for the O-H bonds in the MgO_6 octahedral layer. It is interesting to note that the structure of phase D is isostructural with that of lithium hexafluorozirconate, Li_2ZrF_6 (Brunton 1973), and many other similar compounds, such as Cr_2UO_6 and Li_2NbF_6.

In spite of the existence of 5.5% Mg in the Si site, the Si-O bond length (1.805 Å) in phase D is very comparable with those found in other high-pressure silicates that contain sixfold-coordinated Si (e.g., Finger et al. 1991; Pacalo and Parise 1992). However, the Si-O distance of 1.805 Å is larger than expected from ionic radii (1.76 Å) and the Mg-O distance (2.105 Å) is also slightly larger than expected (2.08 Å) (Shannon and Prewitt 1969). Owing to the edge sharing, the SiO_6 octahedron is considerably distorted in terms of octahedral angle variance (OAV = 29.2) (Robinson et al. 1971). The shared O-O distance (2.351 Å) in the SiO_6 octahedra is much shorter than the unshared O-O distances (2.611–2.642 Å). The Si-Si distance is 2.740 Å, somewhat longer than that (2.668 Å) between edge-shared SiO_6 octahedra in stishovite (e.g., Ross et al. 1990). Relative to the SiO_6 octahedron, the MgO_6 octahedron is close to a perfect octahedron (OAV = 2.9). It should be noted that the isotropic displacement factor of Mg is anomously large, 2.3 times that of O. This observation is likely to result from the cation-cation repulsion between Mg and H, the short Mg-H distance being only 2.24(6) Å.

All O-H bonding in phase D occurs within the MgO_6 octahedral layer with the short O-H bond of 0.91(5) Å and the longer one of 1.77(5) Å. The O-H-O distance of 2.676 Å is consistent with that estimated from the infrared spectrum (Lu and Hemley, personal communication). In the split H-position model (Model 4) that we adopted in the final refinement, the H-H separation is 0.86(9) Å. It should be noted that the this model can also be thought of as an average of two *P*31*m* structures based on Model 3, in which the O-H bond vectors point in one direction in an MgO_6 layer and the opposite direction in another layer.

The calculated density of phase D is 3.50 g/cm^3, which is substantially greater than any other high-pressure hydrous magnesium silicate found thus far, including phase A (2.96 g/cm^3; Horiuchi et al. 1979), phase B (3.37 g/cm^3; Finger et al. 1991), superhydrous phase B (3.21 g/cm^3; Pacalo and Parise 1992), phase E (2.82 g/cm^3; Kudoh et al. 1993), and phase F (2.85 g/cm^3; Kudoh et al. 1995). The high density of phase D is primarily a consequence of all Si being octahedrally coordinated in the structure.

Calculated X-ray powder diffraction data for phase D are given in Table 3, along with data from Liu (1987) and Ohtani et al. (1997). Among the eight *d* values given by Liu (1987), five strong ones can be indexed on the phase D cell, whereas three weak ones are not observed for phase D. To our knowledge, no one has been successful in indexing the entire powder pattern reported by Liu (1987). Frost and Fei (in preparation) have systematically studied high-pressure phases in the SiO_2-MgO-H_2O system with temperatures ranging from 1000 to 1400 °C and pressures from 16 to 24 GPa; however, they did not detect any phases with *d* values of 9.5, 3.37, and 2.53 Å, as observed by Liu (1987). It should be noted that the *d* values, especially the 9.5 Å value, that cannot be indexed on the basis of the phase D cell have been found for the phase(s) transformed from garnets (pyrope and almandine) at high temperature and pressure by Liu

(1974, 1975), who postulated the origin of these reflections from a possible superstructure of perovskite. Accordingly, we think that the sample studied by Liu (1986, 1987) probably contained more than one phase, and phase G reported by Ohtani et al. (1997) possesses the same structure as that of phase D observed by Liu (1986, 1987).

The measured bulk moduli of phase E and superhydrous phase B are 112 GPa (Bass et al. 1991) and 145 GPa (Kudoh et al. 1994), respectively, whereas values estimated by Kudoh et al. (1995) for phases A, B, E, F, and superhydrous phase B are 97, 163, 122, 130, and 143 GPa, respectively. The bulk modulus of phase D, determined by Frost and Fei (in preparation) from unit-cell volume compression data, is 200(4) GPa, the largest of all high-pressure hydrous magnesium silicates. Li and Jeanloz (1991) synthesized an assemblage of perovskite and phase D from a mixture of $Mg_{0.88}Fe_{0.12}SiO_3$ pyroxene with 4 wt% H_2O at ~40–60 GPa and ~1700 °C, which suggests that phase D is stable under lower mantle conditions. Given its large bulk modulus, high density, large H content, and stability at high temperature and pressure, we conclude that phase D is a prime candidate for H_2O storage in the transition zone and lower mantle.

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