

Elasticity of single-crystal phase D (a dense hydrous magnesium silicate) by Brillouin spectroscopy

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Abstract

Phase D ($\text{MgSi}_2\text{O}_6\text{H}_2$) is the only hydrous magnesium silicate, where all Si atoms are octahedrally coordinated. The single-crystal elastic constants of phase D have been measured by Brillouin spectroscopy at ambient conditions. The elastic constants C_{11} , C_{33} , C_{44} , C_{12} , C_{13} and C_{14} , based on a trigonal unit cell, are 284.4 ± 3.0 , 339.4 ± 9.1 , 120.7 ± 1.9 , 89.4 ± 4.2 , 126.6 ± 3.1 and -4.7 ± 1.4 GPa, respectively. The aggregate adiabatic bulk modulus, using the Voigt-Reuss-Hill (VRH) scheme, is 175.3 ± 14.8 GPa and the shear modulus is 104.4 ± 13.6 GPa. These data yield the compressional-wave velocity, $V_p = 9.70 \pm 0.51$ km/s, and the shear-wave velocity, $V_s = 5.59 \pm 0.36$ km/s, at ambient conditions. Thus, phase D is not only the most closely packed but the least compressible hydrous magnesium silicate known to date.

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1. Introduction

There are several dense hydrous magnesium silicates (DHMS) named as phases A, B, C, D,...that were synthesized at high pressures and high temperatures in various laboratories, see, e.g. [1,2] for reviews. Phase D was discovered and named by Liu [3,4] in the study of the breakdown reaction of serpentine above 220 kbar at ~ 1000 °C. The ideal chemical composition of phase D ($\text{MgSi}_2\text{O}_6\text{H}_2$) was identified in a more detailed study of the phase behavior of serpentine at high pressures and high temperatures [5,6]. According to Yang et al. [7], however, the chemical composition of phase D varies considerably from crystal to crystal with H_2O ranging from 10 to 18 wt% and the Mg/Si ratio from 0.56 to 0.70. The space group of

phase D was determined to be $P\bar{3}1m$ and the hexagonal lattice parameters to be $a = 4.745$ Å and $c = 4.345$ Å on the basis of a single crystal X-ray diffraction study [7]. In the latter study, all Si atoms in phase D were found to be octahedrally coordinated which makes it unique amongst all known DHMS, implying that phase D should be the most closely packed hydrous silicate. It is commonly accepted that the most closely packed compounds should also be least compressible. To verify this, the elasticity of phase D was investigated in the present study.

2. Experimental procedures

Single crystals of phase D, with sizes up to about 80 μm in diameter, were synthesized at 19 GPa at 1000 °C for 100 h, using a stoichiometric $\text{MgO-SiO}_2\text{-Mg(OH)}_2$ mixture, in a multi-anvil press at the Universita Studi Degli di Milano, Italy. After synthesis, phase D was identified by both Raman and X-ray diffraction studies, and the

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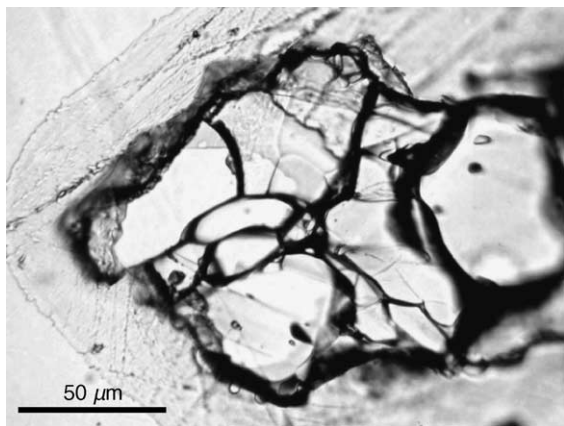


Fig. 1. A photo of the aggregate platelet of the sample of phase D used in the present study.

hexagonal lattice parameters were measured as $a = 4.759 \pm 0.005 \text{ \AA}$ and $c = 4.355 \pm 0.007 \text{ \AA}$ with a microfocus X-ray diffractometer at Tokyo Institute of Technology. Electron microprobe analysis indicated that the chemical composition of phase D was $\text{Mg}_{1.02}\text{Si}_{1.71}\text{O}_6\text{H}_{3.12}$ with $\text{H}_2\text{O} = 16.3 \text{ wt\%}$ and $\text{Mg/Si} = 0.60$. Thus, the density of the present sample of phase D is calculated to be $3.34 \pm 0.01 \text{ g/cm}^3$.

Because of the small crystal size, the samples have been prepared in several different ways. A sample prepared from an aggregate that is composed of several single crystals of phase D was proved to be the most satisfactory for our purposes. Two opposite sides of this aggregate were polished to be parallel to each other within $\pm 10'$ as a single platelet (see Fig. 1). This aggregate platelet produced a Brillouin spectrum of phase D without the interference from either the cover glass or glue (see Fig. 2). Using the same aggregate platelet, we were able to collect Brillouin spectra from several different single crystals of phase D that

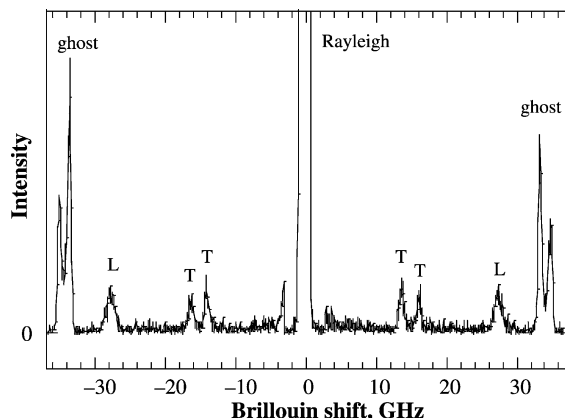


Fig. 2. A representative Brillouin spectrum of phase D. *L* and *T* indicate the longitudinal and transverse modes, respectively. The spectrum was collected in a phonon direction of $(-0.030, 0.727, -0.687)$ at a χ angle of 60 degrees.

presented different crystallographic planes to the laser beam. Brillouin spectra were also collected with the two sides of the aggregate platelet reversed to reduce possible errors introduced by non-parallelism of the platelet faces.

The aggregate platelet was about $30 \mu\text{m}$ in thickness and was mounted on an Eulerian cradle, which was used to control the sample orientation on the Brillouin system. An argon ion laser ($\lambda = 514.5 \text{ nm}$) with 80–100 mW of power and a six-pass tandem Fabry–Pérot interferometer were used for the Brillouin experiments. Our Brillouin experiment utilizes a symmetric scattering geometry with an external angle between the incident and scattered beams of 90° , which yields acoustic velocity measurements independent of the refractive index of the specimen and the Brillouin frequency shift $\Delta\omega$ is directly related to the acoustic velocity V and the incident laser wavelength λ by

$$V = \frac{\Delta\omega\lambda}{\sqrt{2}} \quad (1)$$

A Brillouin spectrum consists of an elastically scattered component with the same frequency as the excitation source and a set of inelastically scattered components. The latter display a frequency shift caused by the interaction between photons and phonons in the sample. Details of the Brillouin scattering technique have been widely elucidated in the literature, e.g. [8,9]. The birefringence of non-isotropic crystals can be problematic when utilizing Eq. (1), because birefringence can yield double peaks or cause peak broadening in the Brillouin spectrum. As can be seen from Fig. 2, the Brillouin peaks of phase D are generally sharp. Therefore, possible errors introduced by the birefringence of phase D should be minor. The details of this issue have also been elucidated earlier [8,9].

3. Results and discussion

Although the data have been collected from several independent crystals, for a given crystallographic plane, most of the data are incomplete. This is due to the scarceness of data points on the same plane, as a result of interference by the cover glass and/or glue, or from being terminated by laser damage. However, the data obtained from one particular crystallographic plane yielded satisfactory results. In order to enhance the reliability of the data, more measurements on this plane were undertaken. The normal vectors for this plane of phase D, after a series of iterated calculations (see below), had been determined to be $(0.208, 0.676, 0.707)$. It has been demonstrated that from measurements in a single crystallographic plane, it is possible to deduce the nine complete elastic constants C_{ij} for orthorhombic crystals [10,11]. Phase D belongs to the trigonal system, and it requires only six or seven (depending upon the space group) elastic constants to completely describe its elastic properties. Calcite also belongs to the trigonal

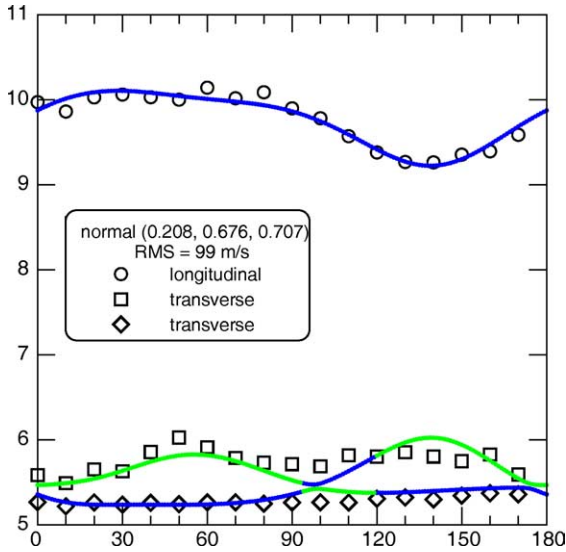


Fig. 3. Longitudinal and transverse velocities as a function of χ angle, which is about an arbitrary setting mark on the three-circle Eulerian cradle, for phase D. Normal vectors relative to the Cartesian system for the crystallographic plane are also shown, together with the root-mean-square deviations between calculated and measured velocities. Solid lines are velocity predictions from the best-fitting elastic constants C_{ij} 's obtained in this study, and vertical bars give the uncertainties for individual velocity measurements.

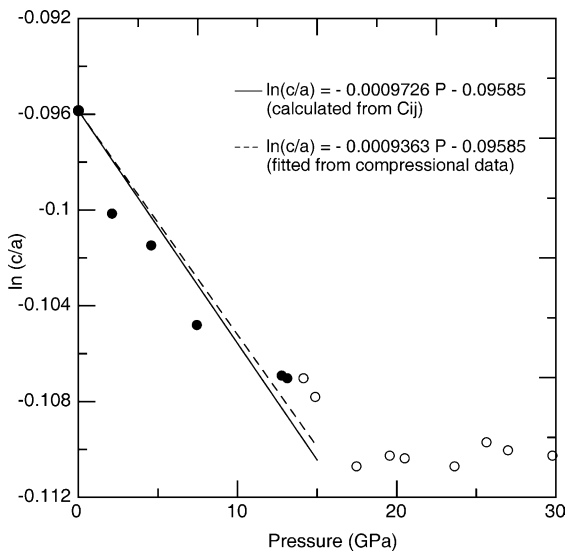


Fig. 4. Logarithmic axis ratio c/a for phase D as a function of pressure. Solid and open symbols (distinguished by the present study) are experimental data reported by Frost and Fei [15]. In order to compare to our ambient data, only the data marked by solid symbols below about 14 GPa were used to fit a linear regression (the dotted line). The solid line was derived from Eq. (2) using the S_{ij} 's obtained in this study.

system, and we have previously determined its elastic constants based on one crystallographic plane using Brillouin spectroscopy [9].

The measured acoustic velocities of the co-planar orientation are illustrated in Fig. 3 for the chosen platelet of phase D. The final data sets of phase D for elasticity inversion consisted of 54 mode velocity determinations (Fig. 3), and all of these are averages of three or more redundant measurements in each direction to ensure the reproducibility of the Brillouin signals. A least-squares algorithm was used to calculate the normal vectors of the crystal and to fit the orientation of phonon directions with an estimated accuracy of better than two degrees. The systematical difference between the calculated line and the experimental data is shown in Fig. 3 and is similar to those reported earlier [8,9]. On the basis of the velocity data and the fitted phonon directions, we used a non-linear inversion procedure to solve the six elastic constants of trigonal phase D. The non-linear inversion procedure uses the Gauss–Newton algorithm with Levenberg–Marquardt modifications for global convergence of solutions, and has been widely adopted for finding solutions to the Christoffel equations, e.g. [12]. Although it is possible that the effect of uncertainties on the phonon directions might be amplified in solving the elastic constants [13], the final estimation of both the phonon directions and the elastic constants (plus the face normal vector) converged to a statistical minimum after several iterations.

The elastic constants of phase D obtained in this study are 284.4 ± 3.0 , 339.4 ± 9.1 , 120.7 ± 1.9 , 89.4 ± 4.2 , 126.6 ± 3.1 and -4.7 ± 1.4 GPa for C_{11} , C_{33} , C_{44} , C_{12} , C_{13} and C_{14} , respectively. Our Brillouin data of elastic constants of phase D may be compared with the static compression data of phase D reported by Frost and Fei [14, 15] and Kudoh et al. [16], who utilized a diamond-anvil cell and synchrotron X-ray diffraction. The logarithmic pressure derivative of the axial ratio c/a for a hexagonal crystal is related to the elastic compliance s_{ij} , or the inverse of elastic constants, as follows [17]:

$$\frac{d \ln(c/a)}{dP} = s_{11} + s_{12} - s_{13} - s_{33} \quad (2)$$

Fig. 4 displays the c/a ratio of phase D as a function of pressure reported by Frost and Fei [15]. Our elastic constants of phase D yield a logarithmic pressure derivative for the c/a ratio of $-9.73 \times 10^{-4} \text{ GPa}^{-1}$, which is shown as a solid line in Fig. 4. This value is in good agreement with the c/a data measured in the compression study of phase D below 14 GPa (note that only the compression data at lower pressures are compared because our data were determined at ambient conditions and only the initial slope of the variation can be constrained).

The aggregate adiabatic bulk modulus for phase D, calculated using the Voigt-Reuss-Hill (VRH) averaging scheme, is $B_{\text{VRH}} = 175.3 \pm 14.8$ GPa and the shear modulus is $G_{\text{VRH}} = 104.4 \pm 13.6$ GPa. Frost and Fei [14] obtained an

Table 1
Ambient values of B_{VRH} , G_{VRH} and density (ρ) for all DHMS materials known

Materials	B_{VRH} (Gpa)	G_{VRH} (Gpa)	ρ (g/cm ³)	References
Phase C (Mg ₁₀ Si ₃ O ₁₈ H ₄)	154	97	3.327	[18]
Phase D (Mg _{1.02} Si _{1.71} O ₆ H _{3.12})	175	104	3.34	This study
Hydrous β -phase ^a (Mg _{1.75} SiO ₄ H _{0.5})	155		3.33	[19]
Hydrous γ -phase (Mg _{1.89} Si _{0.97} O ₄ H _{0.33})	160	106	3.45	[20,21]

^a The value of B_{T} is given instead.

isothermal bulk modulus $B_{\text{T}}=200\pm 7$ GPa in their non-hydrostatic compression study of phase D, Frost and Fei [15] obtained $B_{\text{T}}=166\pm 3$ GPa in their hydrostatic-and-quasihydrostatic compression study of phase D, and Kudoh et al. [16] yielded $B_{\text{T}}=150\pm 4$ GPa based on three high-pressure data points. Considering that the values of B_{T} were derived by fitting compression data to an empirical equation of state with a poorly constrained value of B' , the agreement in the values of B' s obtained between the compression studies and the present measurement is reasonably good.

The aggregate compressional velocity V_{p} , shear velocity V_{s} , and bulk sound velocity $V_{\text{\phi}}$ of phase D are calculated from the following equations;

$$V_{\text{p}} = [(B + 4/3G)/\rho]^{1/2} = 9.70 \pm 0.51 \text{ km/s} \quad (3)$$

$$V_{\text{s}} = [G/\rho]^{1/2} = 5.59 \pm 0.36 \text{ km/s} \quad (4)$$

$$V_{\text{\phi}} = [B/\rho]^{1/2} = 7.24 \pm 0.32 \text{ km/s} \quad (5)$$

So far, the complete elastic constants are available for only three DHMS materials. The ambient values of B_{VRH} , G_{VRH} , and density for all these materials are shown in Table 1 (ambient values of B_{T} and density for the hydrous β -phase are also shown for comparison). Table 1 shows that phase D possesses the highest value of B_{VRH} among all the DHMS, because it is the most closely packed DHMS. Thus, phase D is the least compressible hydrous magnesium silicate known to date.

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References

- [1] L. Liu, Trends in Mineralogy, Vol. 2, Research Trends, Trivandrum, 1998, p. 57.
- [2] Q. Williams, R.J. Hemley, Annu. Rev. Earth Planet. Sci. 29 (2001) 365.
- [3] L. Liu, Phys. Earth Planet. Int. 42 (1986) 255.
- [4] L. Liu, Phys. Earth Planet. Int. 49 (1987) 142.
- [5] T. Irifune, K. Kuroda, N. Funamori, T. Uchida, T. Yagi, T. Inoue, N. Miyajima, Science 272 (1996) 1468.
- [6] K. Kuroda, T. Irifune, in: M.H. Manghnani, T. Yagi (Eds.), High Pressure–Temperature Research: Properties of Earth and Planetary Materials, AGU, Washington, DC, 1998, p. 545.
- [7] H. Yang, C.T. Prewitt, D.J. Frost, Am. Miner. 82 (1997) 651.
- [8] S.V. Sinogeikin, J.D. Bass, Phys. Earth Planet. Int. 120 (2000) 43.
- [9] C.C. Chen, C.-C. Lin, L. Liu, S.V. Sinogeikin, J.D. Bass, Am. Miner. 86 (2001) 1525.
- [10] T.S. Duffy, C.S. Zha, R.T. Downs, H.K. Mao, R.J. Hemley, Nature 378 (1995) 170.
- [11] C.S. Zha, T.S. Duffy, H.K. Mao, R.T. Downs, R.J. Hemley, D.J. Weidner, Earth Planet. Sci. Lett. 147 (1997) E9.
- [12] C.S. Zha, T.S. Duffy, R.T. Downs, H.K. Mao, R.J. Hemley, J. Geophys. Res. 101 (1996) 17535.
- [13] A.G. Every, Phys. Rev. B22 (1980) 1746.
- [14] D.J. Frost, Y. Fei, J. Geophys. Res. 103 (1998) 7463.
- [15] D.J. Frost, Y. Fei, Phys. Chem. Miner. 26 (1999) 415.
- [16] Y. Kudoh, T. Kuribayashi, H. Mizobata, E. Ohtani, EOS (AGU) 80 (1999) F938.
- [17] J.F. Nye, Physical Properties of Crystals, Oxford University Press, London, 1957.
- [18] R.E.G. Pacalo, D.J. Weidner, Phys. Chem. Miner. 23 (1996) 520.
- [19] H. Yusa, T. Inoue, Geophys. Res. Lett. 24 (1997) 1831.
- [20] T. Inoue, D.J. Weidner, P.A. Northrup, J.B. Parise, Earth Planet. Sci. Lett. 160 (1998) 107.
- [21] J. Wang, S.V. Sinogeikin, T. Inoue, J.D. Bass, Am. Miner. 88 (2003) 1608.