

The equation of state of forsterite to 17.2 GPa and effects of pressure media

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ABSTRACT

Pressure-volume X-ray diffraction data were collected at eight pressures to 17.2 GPa for synthetic single-crystal forsterite, Mg_2SiO_4 . Birch-Murnaghan equation-of-state parameters were determined to be $K_0 = 125(2)$ GPa and $K'_0 = 4.0(4)$. To ensure hydrostatic conditions, we monitored the diffraction-peak shapes while the sample was in different pressure media: 4:1 methanol-ethanol, He, and Ar. The diffraction peaks for forsterite in 4:1 methanol-ethanol at 12.2 GPa were broadened to such an extent that we believe that any data collected at similar pressures and in this medium may be suspect and should be examined critically. The diffraction-peak profiles for the sample in He were sharp and well-formed, suggesting He provides an excellent medium at pressures ≤ 17.2 GPa. However, upon decompression, the diffraction peaks of the sample in He also showed significant broadening. This broadening suggests that with increasing pressure He diffused into the crystal, but with the release of pressure the He was unable to diffuse out quickly. The diffraction peaks regained their sharpness after several months.

INTRODUCTION

Forsterite, Mg_2SiO_4 , is an important constituent of the Earth's upper mantle. Mg-rich olivines $[(\text{Mg},\text{Fe})_2\text{SiO}_4]$ are found abundantly in mantle-derived rocks such as peridotites and are major components of upper-mantle mineralogical models (Ringwood 1975; Duffy and Anderson 1989; Ita and Stixrude 1992). The 410 km seismic discontinuity is believed to be caused largely by the transformation of olivine to the β -phase wadsleyite. Olivine, however, may persist metastably to transition-zone pressures ($P > 13.8$ GPa) in subducting slabs where its eventual transformation could be the cause of deep-focus earthquakes (Green 1994). Equation-of-state properties of forsterite are critically important for the evaluation of mantle composition by comparison of various mineralogical models with seismic velocity profiles (Duffy et al. 1995).

We recently conducted a study to determine the elastic contents of single-crystal forsterite at pressures between 3 and 16 GPa in a diamond-anvil cell using Brillouin spectroscopy (Zha et al. 1994). As part of the study, the density and orientation of the crystals were measured by X-ray diffraction methods at eight pressures using three pressure media. This paper reports our findings for the pressure-volume equation of state and the effects of different pressure media.

EXPERIMENTAL METHODS

A large, colorless crystal of synthetic forsterite was obtained from H.S. Yoder Jr. of the Geophysical Laboratory. The crystal had been synthesized, apparently near the turn of the century, by fusing magnesia, silica, and

magnesium chloride in an atmosphere of HCl at approximately 1000 °C (Allen et al. 1906). We determined that the crystal was pure Mg_2SiO_4 using a JXA-8900L electron probe microanalyzer.

All X-ray diffraction studies were conducted on a Picker four-circle diffractometer operated at 45 kV and 40 ma with $\text{MoK}\alpha$ radiation ($\lambda = 0.7093$ Å). The ambient-pressure cell parameters of a $130 \times 90 \times 60$ μm fragment were refined from the positions of 26 reflections ($24^\circ \leq 2\theta \leq 35^\circ$) using the method of Ralph and Finger (1982) and are listed in Table 1. Profiles of diffraction intensities indicated that the peaks were sharp and well formed with full widths at half maximum between 0.10 and 0.15 in ω . A representative peak profile, 131, is plotted in Figure 1.

A small fragment, $80 \times 60 \times 15$ μm , was loaded into a modified Merrill-Bassett cell (Mao and Bell 1980). The sample was ground and polished so that the axis of the diamond cell made equal angles with the forsterite unit-cell axes [i.e., the crystal was polished perpendicular to the reciprocal direction vector ($|a| |b| |c|$)]. This particular orientation ensured sufficient access to reciprocal space so that a sufficient number of sound-wave velocities could be measured by Brillouin scattering using data from only one crystal (Zha et al. 1994). The cell consisted of a 0.3 carat diamond with a 600 μm culet mounted on high-speed steel seats, a 50 μm thick rhenium gasket with a 250 μm hole, and a pressure medium of methanol-ethanol in a ratio of four parts to one part by volume. Fragments of ruby with maximum dimension < 10 μm provided an internal pressure calibrant, as described by Hazen and Finger (1982). The pressure was measured at 9.6 GPa, and cell parameters were refined from the positions of all strong and accessible reflections ($10^\circ \leq 2\theta \leq 31^\circ$) (Table

TABLE 1. Forsterite cell-parameter data

<i>P</i> (GPa)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	Media
0.00	4.7565(12)	10.1982(11)	5.9829(10)	290.22(9)	—
3.1(1)	4.7248(15)	10.0702(23)	5.9264(15)	281.97(11)	Ar
6.1(1)	4.7102(11)	9.9966(20)	5.8872(13)	277.21(8)	Ar
9.6(1)	4.6878(14)	9.9195(29)	5.8457(23)	271.83(12)	meth.- eth.
10.5(1)	4.6726(35)	9.9052(47)	5.8293(33)	269.80(22)	He
15.1(1)	4.6521(17)	9.7604(38)	5.7834(19)	262.60(12)	He
16.2(1)	4.6497(26)	9.7294(53)	5.7681(21)	260.95(17)	He
17.2(1)	4.6411(18)	9.7100(42)	5.7630(19)	259.72(13)	He

Note: Birch-Murnaghan equation-of-state parameters: $V_0 = 290.14(9)$ Å³, $K_0 = 125(2)$ GPa, $K' = 4.0(4)$.

1). Profiles of diffraction intensities indicated that the peaks were sharp and well formed.

The pressure was then increased to 12.2 GPa and diffraction profiles were examined; the width of the 131 peak was 1.0° (Fig. 1). Cell parameters were not refined. Pressure was released and the peak was reexamined, displaying a width of 0.4° after 15 min and 0.13° after ~ 12 h. The same crystal was loaded again into the diamond-anvil cell, but, in this case, a He pressure medium was added using a gas-loading apparatus. Cell parameters were refined at pressures of 10.5, 15.1, 16.2, and 17.2 GPa (Table 1) from the same set of reflections as measured earlier. Peak profiles were sharp at all these pressures, as indicated by the representative 131 profile in Figure 1 at 17.2 GPa.

The pressure was decreased to 6 GPa, but the peak profile was considerably broadened, as illustrated in Figure 2. The pressure was then released, and the profile was measured in air after an elapsed period of 4 months (Fig. 2). The main peak regained its sharpness, but a second, broader peak appeared concurrent with, and presumably due to, a new crack in the crystal that separated it into two slightly misoriented fragments. Two months later the peak was measured again. The main peak and the second peak were both sharp and well formed, indicating that the He had diffused out of both fragments.

A different fragment from the same crystal, $120 \times 100 \times 50 \mu\text{m}$, was polished to nearly the same orientation and loaded into the cell with Ar as the pressure medium. Cell parameters were obtained at 3.1 and 6.1 GPa (Table 1). Ar was chosen because the Brillouin peaks of He obscure those of forsterite in this pressure region, precluding the use of He as a medium at low pressures in our related study to determine the elastic constants of forsterite at high pressure (Zha et al. 1994). The X-ray diffraction peak profiles remained sharp at both 3.1 and 6.1 GPa while using Ar as a pressure medium. Bell and Mao (1981) suggested that Ar is useful as a hydrostatic pressure medium to about 9 GPa.

EFFECTS OF PRESSURE MEDIA

An examination of the 131 peak profile in Figure 1 indicates the quality of diffraction significantly deterio-

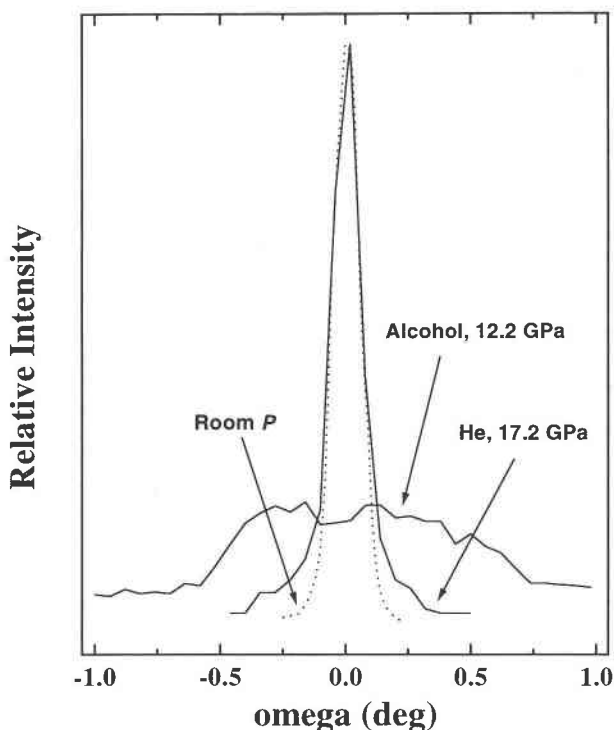


FIGURE 1. Three profiles of the 131 diffraction peak of forsterite. The dotted line is the profile at room pressure, the narrow solid curve is the profile at 17.2 GPa in a medium of He, and the broad solid curve is the profile at 12.2 GPa in 4:1 methanol-ethanol.

rated for the forsterite crystal in a 4:1 methanol-ethanol pressure medium between 9.6 and 12.2 GPa. Piermarini et al. (1973) reported that freezing of this pressure medium occurs around 10 GPa at ambient temperature, and so it is likely that the poor quality of the diffraction profile is a result of strain induced in the crystal by the freezing of methanol-ethanol. The restoration of peak quality that was observed upon the release of pressure in the diamond cell is indicative of elastic strain.

On the other hand, the 131 peak shape remained quite sharp (except for the increase in diffuse scattering indicated by broadening of the base) up to 17.2 GPa when the crystal was immersed in He. This observation suggests that, in contrast to methanol-ethanol, a He medium maintains a nearly hydrostatic environment, at least up to this pressure. Although He freezes at 11.6 GPa, its bulk modulus is very small, $K_0 = 0.225$ GPa (Loubeyre et al. 1993), and its low rigidity allows quasi-hydrostatic conditions to be maintained to high pressure. Bell and Mao (1981) suggested that He is suitable as a pressure-transmitting medium at all pressures up to at least 60 GPa.

Upon decompression to 6 GPa in the He medium, the peak shape broadened considerably, and, subsequently, after the crystal was removed from the diamond cell, the crystal cracked as well. These phenomena may indicate that He penetrated the crystal as the pressure was increased and was unable to diffuse out quickly when pres-

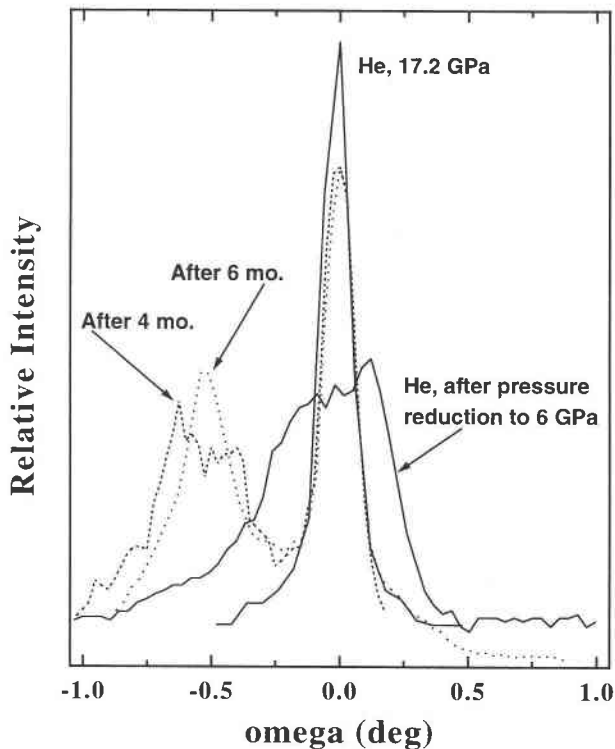


FIGURE 2. Profiles of the 131 diffraction peak of forsterite. The solid narrow curve is the profile at 17.2 GPa, and the broad solid curve is the profile at 6 GPa, both in a medium of He. The long- and short-dashed curves are the same crystal measured in air 4 and 6 months later, respectively.

sure was released. Consequently, the internal pressure in the crystal, generated by thermal vibrational effects of He, exceeded the external pressure, and, because of the intrinsic anisotropy of the olivine structure and the assumed nonhomogeneous distribution of He within it, the diffraction peaks were distorted and broadened. Preexisting defects or internal flaws might have made our crystal particularly susceptible to the effects of the He, leading to the cracking.

The fact that the peak shapes returned to their original sharpness after ~ 6 months suggests that the He eventually escaped from the forsterite crystal. A similar phenomenon was observed in silica glass released from a Ne medium at 0.5 GPa. The glass was observed to emit bubbles of Ne for 2 d after removal from the cell (H.K. Mao, personal communication). Therefore, as a caveat, even though He offers what appears to be an excellent pressure medium, measurements should not be made on a sample after the pressure has been reduced until a sufficient amount of time has elapsed to allow the He to escape. Heating the sample may shorten this waiting period.

Incidentally, after the X-ray measurement at 6 GPa but before the cracking, the sample was removed from the diamond cell with the He medium and remounted in an Ar medium. Brillouin data collected at 6 GPa in the Ar medium were anomalous and indicated a large decrease

in anisotropy of the sound-wave velocities. It remains to be determined whether He that diffuses into a crystal has any effect on the values of K_0 and K'_0 .

In this study we were unable to determine whether the He created any systematic, homogeneous deformation of the structure at high pressure. However, in their study of the structure of cordierite as a function of pressure, Koepke and Schulz (1986) observed structural differences that were attributed to the presence of pressure media in the structure. They used water and fluorocarbon as media at 2.3 and 2.2 GPa, respectively. The unit-cell volumes of cordierite in H_2O were systematically larger than those in fluorocarbon. Koepke and Schulz (1986) suggested that H_2O entered the cordierite channels at high pressure, but fluorocarbons, too large for the channels, did not. Furthermore, difference-Fourier maps also indicated the presence of H_2O within the channels.

It is clear that He diffuses into the crystal at high pressures but whether it occupies defects or actually enters the lattice is not established. Experiments in our laboratory have demonstrated that diamond anvils that are not of the highest quality have a tendency to break along defects upon pressure release if He is used as the pressure medium. If the diamonds are of high quality with no visible defects, they can be reused over and over again as anvils. On the basis of this evidence and the sharpness of the 131 peak profile at 17.2 GPa (Fig. 1) we believe He occupies defects in the forsterite crystal and is not a source of lattice distortions until pressure release.

AXIAL COMPRESSIBILITIES AND EQUATION OF STATE

The compression of the unit cell of forsterite is anisotropic. Compressibilities [$\beta_a = (1/a)(da/dP)$, etc.] of a , b , and c are 1.354, 2.700, and $2.101 \times 10^{-3} \text{ GPa}^{-1}$, respectively, as determined from linear fits of the cell dimensions vs. pressure. The relative axial compressibilities for $a:b:c$ are then 1:1.99:1.55. It may be possible that the a and c cell dimensions require second-order terms in pressure to provide the best fit to the data; however, the present data are insufficient to demonstrate this conclusively.

The pressure-volume data of Table 1 were fitted, using a Levenberg-Marquardt algorithm (Press et al. 1986), to a third-order Birch-Murnaghan equation of state to yield $V_0 = 290.14(9) \text{ \AA}^3$, $K_0 = 125(2) \text{ GPa}$, and $K'_0 = 4.0(4)$, where the numbers in parentheses are uncertainties of one standard deviation. These values are in excellent agreement with our preliminary Brillouin scattering results, which yield an isentropic bulk modulus and pressure derivative of $K_{0S} = 129(1) \text{ GPa}$ and $K'_{0S} = 4.2(2)$. Previous determinations of the bulk modulus of forsterite from ambient-pressure elasticity data yielded $K_0 = 128(1) \text{ GPa}$ when corrected from adiabatic to isothermal conditions (Sumino and Anderson 1984). The data and the fitted curve are plotted in Figure 3 along with pressure-volume data from other experiments (Hazen 1976; Olinger 1977; Kudoh and Takéuchi 1985; Will et al. 1986).

Our data agree well with those reported by Hazen (1976) and Olinger (1977). In both cases the pressure medium

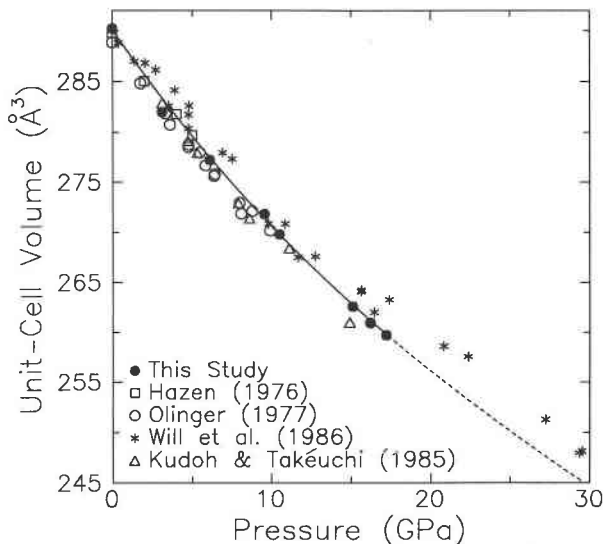


FIGURE 3. Pressure-volume plot of the equation of state of forsterite. The solid line represents the Birch-Murnaghan curve that best fits our data; the dashed curve is an extrapolation to values beyond our highest measured pressure. Other experimental data are plotted for comparison and discussed in the text.

was 4:1 methanol-ethanol, and the pressures were kept lower than 10 GPa. The Olinger (1977) data from powder samples are consistently lower but parallel to the trend of our data because they are based on a value of V_0 that is 1.38 \AA^3 smaller than ours. Fitting a Birch-Murnaghan equation to the data reported in Olinger's study yields $K_0 = 120(6) \text{ GPa}$ and $K'_0 = 5.6(17)$.

Kudoh and Takéuchi (1985) reported significant changes in the slope of the a and b cell dimensions, the volume of the unit cell, and the mean M1-O bond length from data recorded at pressures above 10 GPa. However, they used 4:1 methanol-ethanol as a pressure medium, which, as our study shows, distorts the structure of forsterite. The freezing of the pressure medium and the subsequent induced strain on their forsterite crystal probably caused their observed slope changes. The X-ray peak shapes in their experiment were also considerably broadened at the higher pressures (Y. Kudoh, personal communication).

Will et al. (1986) also used a 4:1 methanol-ethanol mixture as their medium while measuring the diffraction-peak positions with synchrotron radiation at pressures up to 30 GPa. Aside from the large scatter in their data (average errors in volume are 1 \AA^3), their data deviate significantly from our trend at the higher pressures at which the medium is frozen.

Freezing of the pressure medium also would account for the anomalous results of Kudoh and Takeda (1986) in their study of the structure of the olivine phase fayalite, Fe_2SiO_4 , at pressures up to 14 GPa in a medium of 4:1 methanol-ethanol. Their reported coordinates yield Si-O bond lengths that range from 1.4 to 1.8 Å. This is a de-

viation of $\pm 0.2 \text{ \AA}$ from typically reported values of Si-O bond length.

Numerous Raman and infrared spectroscopic studies of forsterite have been reported at elevated pressures (e.g., Hofmeister et al. 1989; Chopelas 1990; Wang et al. 1993; Durben et al. 1993; Liu and Mernagh 1994). Chopelas (1990), in a Raman study using a methanol-ethanol medium, observed discontinuities in several Raman modes and a reduction in intensity of all modes near 9.1 GPa. These results, together with the linear compressibility changes observed by Kudoh and Takéuchi (1985), were interpreted as a consequence of a second-order phase transition or a change in the compression mechanism of forsterite (Chopelas 1990). Similar changes in Raman spectra near this pressure were reported for $\beta\text{-Mg}_2\text{SiO}_4$ compressed in an Ar medium (Chopelas 1991), which also is nonhydrostatic above 9 GPa (Bell and Mao 1981). Other studies, using both methanol-ethanol and Ar media, have also reported slope changes in the pressure-dependence of some Raman modes of forsterite at 7–9 GPa, but no bands were found to disappear (Wang et al. 1993; Durben et al. 1993).

Our results do not provide support for a phase transition or a change in the compression mechanism of forsterite around 9 GPa. As discussed above, the discontinuity observed by Kudoh and Takéuchi (1985) may well be a consequence of the use of a methanol-ethanol pressure medium, which dramatically affects X-ray diffraction peaks above 10 GPa (Fig. 1). When He is used as a pressure medium, no anomalous compressibility is observed up to 17.2 GPa. Liu et al. (1994) and Liu and Mernagh (1994) reported Raman data on forsterite and $\beta\text{-Mg}_2\text{SiO}_4$ to nearly 20 GPa using a mixture of methanol-ethanol and H_2O as the pressure medium. This medium reportedly does not freeze until pressures are higher than 10 GPa (16:3:1 methanol: ethanol: water remains hydrostatic to 14.4 GPa; Fujishiro et al. 1981). They argued that the vibrational frequencies of both methanol-ethanol and water vary nonlinearly with pressure and that no discontinuity is required to fit the data. Thus, at present, there is no strong evidence to support the existence of a structural change in forsterite near 9 GPa at room temperature.

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