Revision 2

Synthesis of large wadsleyite single crystals by solid-state recrystallization

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ABSTRACT

Single crystals of $(Mg_{0.89}Fe_{0.11})_2SiO_4$ wadsleyite with dimensions up to ~1 mm were synthesized by solid-state recrystallization under high pressure. Synthesis experiments of the wadsleyite single crystals were performed at 16 GPa and 1870 K for 1–3 h using a Kawai-type multianvil apparatus. The wadsleyite crystals are virtually free of inclusions and cracks. Their chemical compositions are homogeneous with Fe/(Mg + Fe) of 0.112(2). Unpolarized infrared spectra indicate that the synthesized sample contains 0.15-0.30 wt% H_2O. The method of synthesizing large, high-quality single crystals of wadsleyite will facilitate future measurements of physical properties including elasticity and elastic anisotropy, electrical and thermal conductivities, atomic diffusivity and creep strength, which will improve models of the composition and dynamics of the mantle transition zone.

Keywords: wadsleyite, single crystal, mantle transition zone, high-pressure synthesis, Kawai-type multianvil apparatus

INTRODUCTION

Wadsleyite is expected to be the most dominant mineral at the upper part of the mantle transition zone (MTZ) (e.g. Irifune and Isshiki 1998) and thereby controls the physical and chemical properties of this region. Seismic observations have revealed anisotropic seismic wave propagation within the upper MTZ (e.g. Visser et al. 2008). Global seismic anisotropy in the upper MTZ has been attributed to a crystallographic preferred orientation (CPO) of wadsleyite (e.g. Kawazoe et al. 2013). However, a quantitative evaluation of the seismic anisotropy observed in the upper MTZ is difficult because the elastic stiffness constants C_{ijkl} of wadsleyite have not been experimentally determined under simultaneous high pressure and high temperature (e.g. Wang et al. 2014). Moreover, the wadsleyite CPO in the upper MTZ may cause anisotropy in other physical properties such as viscosity; c.f. deformed olivine in the upper mantle (Hansen et al. 2012). Consequently, a detailed understanding of the anisotropy of the physical properties of wadsleyite is fundamental to model anisotropy of physical and chemical properties in the upper MTZ.

Many types of experiments to determine anisotropy in physical and chemical properties of wadsleyite require single crystals of sufficient size and quality. In experiments with diamond anvil cells (DAC), single crystals larger than 100 μm are useful for the preparation of single-crystal samples with defined dimensions, shape and if needed crystallographic orientation

by the focused ion beam (FIB) technique (Marquardt and Marquardt 2012). In the case of multianvil apparatuses, atomic diffusion and deformation experiments can be performed on wadsleyite samples as small as 0.4–0.5 mm (Kawazoe et al. 2010; Shimojuku et al. 2004). Therefore, wadsleyite single crystals larger than ~0.4 mm are ideal for a range of experiments to determine the anisotropy of its physical properties under high pressure and temperature.

Previously, large wadsleyite single crystals were synthesized by solid-state recrystallization using a Kawai-type multianvil apparatus (Sawamoto 1986). In these experiments, wadsleyite single crystals with dimensions up to 0.5 mm were obtained near the wadsleyite–ringwoodite phase boundary (19–21.5 GPa and 1940–2670 K). However, the wadsleyite crystals contained inclusions and showed variation in Mg/(Mg + Fe) from crystal to crystal (Sawamoto 1986). We note that in this previous study, temperature was overestimated because it has been shown that Mg_2SiO_4 ringwoodite is unstable above ~2170 K (e.g. Fei et al. 2004). In another work, the temperature-gradient method was applied to single-crystal growth of wadsleyite in carbonate solutions using a Kawai-type apparatus (Shatskiy et al. 2009). In these experiments, wadsleyite single crystals with dimensions up to 1.0 mm were obtained in co-existence with quenched melt. However, the carbonate flux method produced crystals with inclusions of the solvent (Shatskiy et al. 2009).

In the present study, we synthesized high-quality single crystals of $(Mg_{0.89}Fe_{0.11})_2SiO_4$ wadsleyite with dimensions up to ~1 mm by solid-state recrystallization. We describe the method and discuss sample characterization including evaluation of inclusions, cracks, chemical compositions and water content. In addition, we outline potential applications for the synthesized crystals to study the intrinsic anisotropy of wadsleyite to many physical and chemical properties.

EXPERIMENTAL METHODS

Synthesis experiments

The starting material was a powder of San Carlos olivine ($(Mg_{0.9}Fe_{0.1})_2SiO_4$). Olivine single crystals with no visible inclusion were hand-picked under a stereomicroscope and ground to a fine powder using a mortar. The starting powder was packed in a Re foil capsule (1.6-mm outer diameter and 2.7-mm length). Neither solvent nor water was added to the starting material.

The high-pressure synthesis was performed using a 1000-ton Kawai-type multianvil apparatus with split-sphere type guide blocks (Keppler and Frost 2005). The second-stage anvils with an 8-mm truncation were made of tungsten carbide (ha-7%, hawedia). The capsule was loaded into a ceramic octahedron with a 14-mm edge length made of semi-sintered Cr-doped

MgO. Pre-formed pyrophyllite gaskets were used. A stepped $LaCrO_3$ furnace was adopted with a ZrO_2 thermal insulator. The ceramic parts of the cell assembly were fired at 1273 K for dehydration. The sample was first compressed to 8.0 MN (815 tonf) at room temperature. Temperature was then increased to 1870 K at rates of ~50-70 K/min. The generated temperature was estimated based on relationships between temperature measured with a thermocouple and electric power to the furnace in separate runs. The uncertainty in temperature is estimated to be ±50 K. The target temperature was held for 1 h (run H4015) or 3 h (run H4150) before rapid quenching. The sample was subsequently decompressed at room temperature for 13-15 h.

Sample analyses

Several crystals from both runs were examined using X-ray diffractometers with a CCD area detector (Oxford Diffraction, Xcalibur2) and a point detector (Huber, SMC9000) operating with Mo *K*α radiation (40 kV and 20-30 mA) for phase identification, verification as singe crystal and orientation. The quality of the crystals was evaluated based on the widths of X-ray diffraction peaks in the final omega scans. Thin sections of the single crystals from run H4015 were examined using a polarization microscope (Leitz, Laborlux 12 Pol S).

The chemical compositions of four crystals were measured using an electron microprobe in wavelength-dispersive mode (JEOL, JXA-8200) operated at 15 kV and 15 nA. Infrared (IR) absorption spectra of three crystals were obtained with a Fourier transform IR spectrometer (Bruker, IFS-120 HR). The crystals were oriented parallel to the (243), (120) or (010) planes and double-side polished to a thickness of 10-13(1) μm using 0.25-μm diamond powder. Unpolarized IR absorption spectra were taken from 4-6 distinct positions on each sample with a spot diameter of about 100 μm. The water contents were determined according to the calibrations by Paterson (1982), Libowitzky and Rossman (1997), and Deon et al. (2010). An orientation factor of 1/3 and a density factor appropriate for Fe-bearing wadsleyite were used for the Paterson (1982) calibration. The total integrated absorption coefficient was multiplied by 3 for the calibrations by Libowitzky and Rossman (1997) and Deon et al. (2010).

RESULTS AND DISCUSSION

High-quality single crystals of wadsleyite with dimensions up to ~1 mm were successfully synthesized at 16 GPa and 1870 K for 1 h (run H4015) or 3 h (run H4150) (Fig. 1). Some single crystals were broken due to cracks caused by decompression. The recovered crystals were identified as wadsleyite by X-ray diffraction. Most of the wadsleyite crystals were free of

118 inclusions and dispersed cracks (Fig. 1c). Uniform extinction upon sample rotation under
119 cross-polarized light further indicated that the crystals were single crystals.

120 The chemical compositions of the wadsleyite crystals are nearly homogeneous within
121 each crystal and among the crystals with Fe/(Mg + Fe) of 0.112(2) (Table 1). The cations per 4
122 oxygens in Table 1 are upper bounds because ~10 % of Fe is expected to be Fe^{3+} in
123 $(Mg_{0.9}Fe_{0.1})_2SiO_4$ wadsleyite synthesized in the Re capsule (Frost and McCammon 2009). The
124 compositions are comparable to those expected in the upper MTZ (Irifune and Isshiki 1998).

125 The unit-cell parameters of wadsleyite from run H4015 were a = 5.7070(9) and
126 5.7069(9) Å, b = 11.4735(11) and 11.4735(10) Å, and c = 8.2741(10) and 8.2740(10) Å when the
127 orthorhombic (the space groups *Imma*, Sawamoto and Horiuchi 1990) and monoclinic (the space
128 group $I2/m$, Smyth et al. 1997) symmetries were assumed, respectively. A β angle of 90.030(11)°
129 was obtained for the monoclinic case. These cell parameters lead to unit-cell volumes of
130 541.78(12) and 541.77(11) $Å^3$, a density of 3.617(7) g/cm^3, and b/a ratios of 2.0104(4) and
131 2.0105(3) for the orthorhombic and monoclinic symmetries, respectively. The average full-width
132 at half-maximum of the final omega scans was 0.082(13)° (Fig. 2) showing the high quality of
133 the crystals.

The water contents of the wadsleyite crystals parallel to the (243), (120), and (010) planes were in the ranges of 0.15(1)-0.20(1), 0.22(2)-0.28(1), and 0.25(1)-0.30(1) wt% H_2O, respectively (Figs. 3 and 4 and Table 2). IR absorption at 3200-3650 cm^{-1} and the water contents are consistent with the one (0.09-0.21 wt%) observed in wadsleyite synthesized from natural olivine powder with no additional water in a previous study (Nishihara et al. 2006). The uncertainty in the water contents given above corresponds to one standard deviation calculated from measurements at 4-6 distinct locations in each single crystal, indicating the homogeneity of the water content (Figs. 3 and 4). The uncertainty in absolute water content is larger than that stated above and can be estimated based on the variation in water content arising from the use of different calibrations (~30 %, Paterson 1982; 10-20 %, Libowitzky and Rossman 1997; 10 %, Deon et al. 2010). The water was supposed to be supplied to the sample from the surrounding ceramics which absorbed moisture from the air after the heating treatment (c.f. Nishihara et al., 2006). This water content is comparable with that estimated for the MTZ (~0.1 wt%, Karato 2011).

Phase transformation kinetics from polycrystalline olivine to wadsleyite likely plays an important role in obtaining the large wadsleyite single crystals by solid-state recrystallization. The small effect of run duration on the maximum dimensions of the synthesized wadsleyite

151 crystals implies that the wadsleyite crystals primarily grew at the beginning of each run (within
152 less than 1 h). Nucleation and growth rates of wadsleyite in polycrystalline olivine significantly
153 decrease and increase with increasing temperature, respectively (Kubo et al. 2004). Therefore,
154 rapid growth of the wadsleyite crystals is expected during the olivine-wadsleyite transformation
155 because of the low nucleation density and high growth rate of wadsleyite in polycrystalline
156 olivine at high temperature.

157

158 **IMPLICATIONS**

159 The large size of the wadsleyite single crystals allows for preparing several samples for
160 the DAC experiments from one single crystal. As an example, we outline the potential use of the
161 crystals to determine C_{ijkl} by Brillouin spectroscopy and single-crystal X-ray diffraction. Two
162 crystals were oriented parallel to the (120) and (243) planes and double-side polished to a
163 thickness of 10 μm (Fig. 1c). Several half disks with a 110-μm diameter were cut from the
164 platelets using a FIB machine (FEI, Scios) operated at 30 kV and 7–30 nA (Fig. 1d). Two half
165 disks with different orientations were loaded with ruby and Sm-doped $Y_3Al_5O_{12}$ chips as pressure
166 calibrants in a sample chamber of a resistively heated DAC equipped with 400-μm culet
167 diamonds. The combined measurement of acoustic velocity distribution in the two chosen

crystallographic planes along with the measurement of unit-cell volume by X-ray diffraction allows for determining all the 9 C_{ijkl} of wadsleyite at the same pressure–temperature conditions (Speziale et al. 2014). The measurement enables us to minimize uncertainties related to different experimental runs, such as the determination of pressure and temperature.

In future studies, the large high-quality single crystals will allow for determining the physical properties of wadsleyite such as sound velocity anisotropy, elasticity, electrical and thermal conductivities, atomic diffusivity, and creep strength. Owing to potential CPO of wadsleyite (e.g. Kawazoe et al. 2013), the upper MTZ can reflect the anisotropic behavior of this phase if the anisotropy in its physical properties is large enough. Consequently, further applications of the grown high-quality wadsleyite single crystals are expected to contribute to the advancement of high-pressure mineralogy.

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FIGURE CAPTIONS

Figure 1. The $(Mg_{0.89}Fe_{0.11})_2SiO_4$ wadsleyite samples synthesized at 16 GPa and 1870 K. (**a**) The sample inside the Re capsule (run H4150). The Re foil was partly removed to show the crystals inside. Two single crystals were also removed at the right part of the sample, and former grain boundaries can be seen as shiny surfaces. The rest of the sample is not shiny because its surface is not smooth due to contact with the capsule wall. (**b**) Examples of the single crystals (run H4150). The crystals look dark because they are thick. Round edges of the crystals reflect the cylindrical shape of the capsule. (**c**) Photomicrograph of a thin section of a single crystal parallel to the (120) plane (run H4015). A few small cracks are visible as gray lines in the left part of the crystal. Note that the whole section does not contain any

large inclusions. (**d**) Backscattered electron image of FIB-cut thin section of the single crystal shown in (**c**).

Figure 3. Unpolarized IR absorption spectra of a $(Mg_{0.89}Fe_{0.11})_2SiO_4$ wadsleyite single crystal synthesized at 16 GPa and 1870 K for 1h (run H4015). The crystal platelet was oriented parallel to the (243) plane. A water content of 0.15(1) wt% H_2O (25000(1000) H/10^6 Si) was deduced from 5 measurements at different locations on the same platelet using the Paterson (1982) calibration. All 5 spectra are plotted in this figure to show homogeneity of the water content in the crystal.

Figure 1a

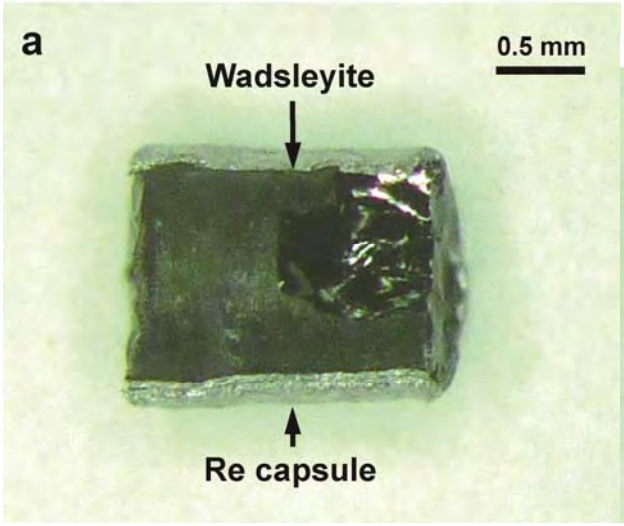


Figure 1b

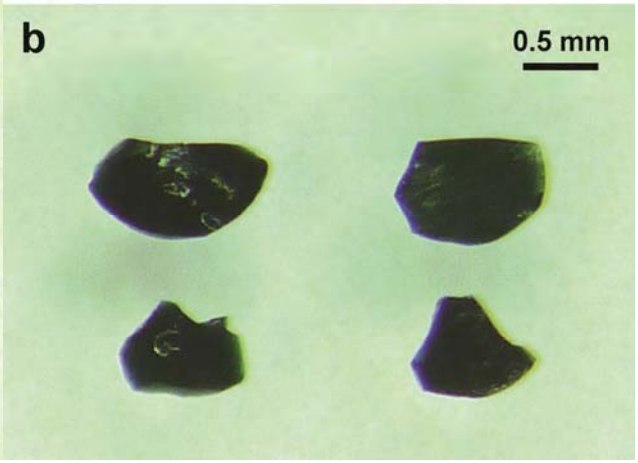


Figure 1c

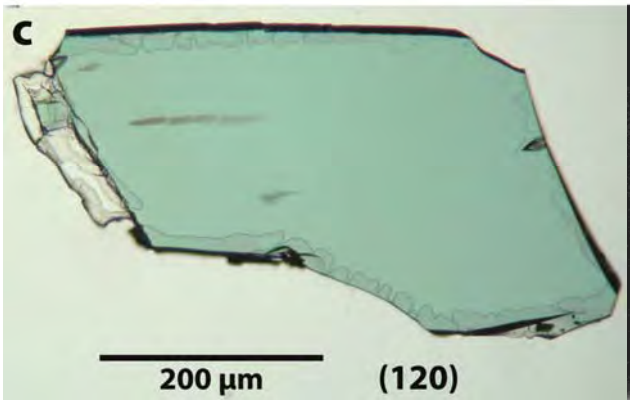


Figure 1d

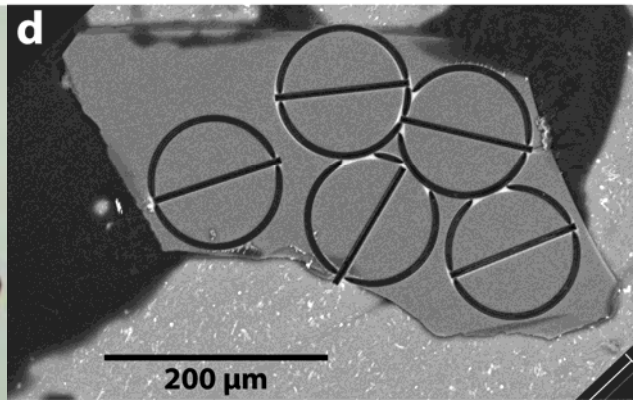
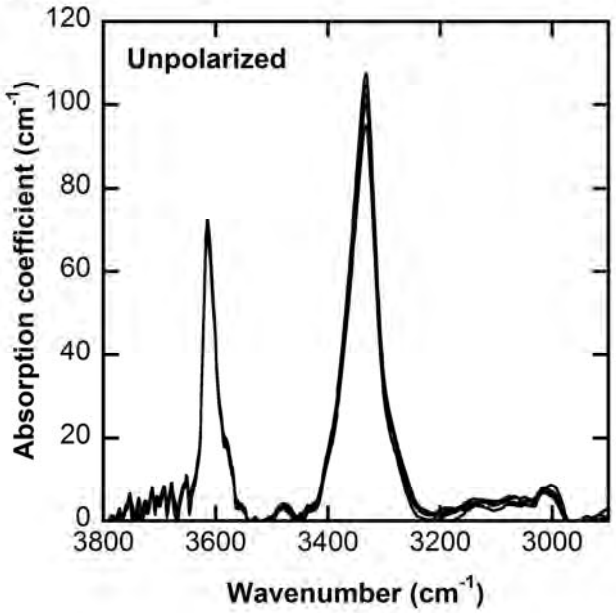


Figure 3



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