



# High-pressure infrared spectroscopy of the dense hydrous magnesium silicates phase D and phase E

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## ARTICLE INFO

### Article history:

Received 4 August 2008

Received in revised form 20 January 2009

Accepted 3 February 2009

### Keywords:

Phase D

Phase E

Infrared spectroscopy

High-pressure

Hydrous phases

## ABSTRACT

Phases D and E are hydrous magnesium silicates that are stable at high-pressure–temperature conditions and could serve as H<sub>2</sub>O carriers in the Earth's mantle, especially in subducting slabs. Using synchrotron infrared (IR) spectroscopy, we measured the infrared spectra of polycrystalline samples of phases D and E to 42 and 41 GPa, respectively. For both phases, at least three broad OH stretch vibrations were observed at elevated pressures indicating that each phase has multiple hydrogen positions that exhibit disorder. No structural phase transition or amorphization was observed for either phase over the measured pressure range. The mode Grüneisen parameters of phases D and E are in the range of  $-0.12$  to  $1.14$  and  $-0.17$  to  $0.83$ , respectively, with mean values of  $0.41$  (phase D) and  $0.31$  (phase E). Using empirical correlations of OH frequency and O···H and O···O bond lengths; the six OH vibrations of phase D at ambient pressure have corresponding O···H and O···O bond distances in the range of  $1.519$ – $1.946$  Å and  $2.225$ – $2.817$  Å, whereas the four OH vibrations of phase E have the corresponding O···H and O···O bond distances in the range of  $1.572$ – $2.693$  Å and  $2.557$ – $2.986$  Å. These ranges encompass values reported from single-crystal X-ray diffraction measurements. At high pressures, the observable OH stretching vibrations exhibit both positive and negative pressure slopes. Our high-pressure infrared spectra for phase D do not support the occurrence of hydrogen symmetrization as predicted by first-principles calculations.

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## 1. Introduction

Hydrogen is a geochemically important element whose abundance is poorly constrained in the Earth's deep interior (Jacobsen and van der Lee, 2006). The presence of hydrogen even in small quantities can affect phase relations, melting temperature, rheology, and other key properties of the deep Earth (e.g., Wood and Corgne, 2007; Williams and Hemley, 2001). Dense hydrous magnesium silicates (so-called alphabet phases) are a class of hydrous silicates that form under high-pressure–temperature conditions in the MgO–SiO<sub>2</sub>–H<sub>2</sub>O system (Williams and Hemley, 2001; Smyth, 2006). These silicates are potentially important components of the deep Earth water cycle especially in cold slab environments (e.g., Liu, 1986, 1987; Kanzaki, 1991; Shieh et al., 1998; Frost, 1999; Kawamoto, 2004; Ohtani et al., 2004; Komabayashi and Omori, 2006). In particular, phase E is likely to be an important water carrier near the base of the upper mantle and the transition zone (Stalder and Ulmer, 2001; Litasov and Ohtani, 2003). Phase D may

be the major H<sub>2</sub>O-bearing phase at the top of the lower mantle in low-temperature slab environments for peridotite compositions (Ohtani et al., 2001, 2004; Komabayashi and Omori, 2006).

High-pressure measurements of vibrational spectra of phases D and E have proven to be challenging. Williams (1992) observed two weak modes in the OH stretching region of the infrared (IR) spectrum from a sample of pyroxene and water that had been laser heated at 32–34 GPa, possibly producing phase D. At ambient pressure, Raman spectra of phase D have been reported by Liu et al. (1998), Frost and Fei (1998), Ohtani et al. (1997), and Xue et al. (2008). For phase E, Raman spectra have been reported at ambient pressures in several studies (Mernagh and Liu, 1998; Frost and Fei, 1998; Shieh et al., 2000a,b) and at high pressures up to 19 GPa by Klepepe et al. (2001). For the IR measurement of phase E, only very weak ambient pressure spectra have been reported to date (Mernagh and Liu, 1998).

Phase E has the ideal formula of Mg<sub>2</sub>SiO<sub>2</sub>(OH)<sub>4</sub> but is highly disordered and exhibits variable Mg/Si ratios and hydrogen contents. The phase has rhombohedral symmetry ( $R\bar{3}m$ ) with Si in tetrahedral and Mg in octahedral coordination; the MgO<sub>6</sub> octahedra form brucite-type layers cross-linked by a layer with a mixture of MgO<sub>6</sub> octahedra, SiO<sub>4</sub> tetrahedra and vacancies (Kudoh et al., 1993). All

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oxygens are equivalent but there are two distinct Mg octahedra and the Si tetrahedron is highly distorted. The structure lacks long-range order. Charge balance is maintained locally by protonation, and a range of Mg/Si ratios and hydrogen contents can be found in phase E.

Phase E can be synthesized from hydrous olivine and serpentine at 13–17 GPa and high temperature (Shieh and Ming, 1996; Irifune et al., 1998; Stalder and Ulmer, 2001). Powder X-ray diffraction studies show that it remains crystalline to at least 42 GPa (Shieh and Duffy, 2003; Shieh et al., 2000a,b). Raman spectra at ambient pressure show broad peaks, consistent with considerable structural disorder (Frost and Fei, 1998; Kleppe et al., 2001). Raman measurements reported three OH vibrations at 2492, 3429, and 3617  $\text{cm}^{-1}$ , but the mode at 2492  $\text{cm}^{-1}$  could only be detected at ambient conditions (Kleppe et al., 2001). The OH mode at 3429  $\text{cm}^{-1}$  broadened with pressure and reached a peak width twice its initial value at pressure of 19 GPa.

Phase D has an ideal formula of  $\text{MgSi}_2\text{O}_4(\text{OH})_2$  and crystallizes in the trigonal system (space group  $P\bar{3}1m$ ). This phase is also disordered with variable Mg/Si ratios and hydrogen contents of 10–18 wt%  $\text{H}_2\text{O}$  (Yang et al., 1997). Ambient-pressure Raman spectra show broad peaks for both lattice and OH modes (Ohtani et al., 1997; Frost and Fei, 1998). Phase D has all silicon in octahedral coordination and is stable to 70 GPa at room temperature (Frost and Fei, 1998; Shieh, unpublished data).

The structure consists of alternating layers of  $\text{MgO}_6$  and  $\text{SiO}_6$  octahedra stacked along the  $c$  direction. In the  $\text{SiO}_6$  layers, the octahedra share edges forming brucite-like layers but 1/3 of the octahedral sites are vacant. The  $\text{MgO}_6$  octahedra are oriented above and below the vacant sites and share corners with  $\text{SiO}_6$  octahedra. Two-thirds of the sites are vacant in the Mg octahedral layer. The  $\text{SiO}_6$  octahedra are distorted as the O–O distance along the shared edge is much shorter than those along the unshared edges (Yang et al., 1997), and this is supported by recent NMR spectroscopy measurements (Xue et al., 2008). The  $\text{MgO}_6$  octahedra show little distortion.

Synthesized phase D samples have Mg/Si ratios ranging from about 0.55 to 0.71 indicating excess Mg and/or deficient Si. Based on recent NMR data, it is proposed that there are both Si vacancies and substitution of Mg into Si sites (Xue et al., 2008) with H providing charge balance. The partially occupied disordered H bond positions are proposed to be located within the Mg octahedral layer and bonded to oxygens of the Si octahedra (Yang et al., 1997; Xue et al., 2008). Phase D is the same phase as the other reported hydrous phases G and F (Ohtani et al., 1997; Kanzaki, 1991), although the Mg/Si ratio and  $\text{H}_2\text{O}$  content vary with synthesis conditions.

Infrared spectroscopy using a synchrotron source is a powerful tool for studying hydrogen-bearing materials at high pressures. Such studies provide insights into phase stability and hydrogen bonding and their pressure dependence. Vibrational spectra also provide insights into thermodynamic properties such as entropy, heat capacity, and thermal expansivity through modeling the contribution of vibrational frequencies to these quantities (e.g., Cynn et al., 1996). In this study, we used high-pressure synchrotron infrared spectroscopy to investigate both phases E and D to pressures above 40 GPa.

## 2. Experimental method

Phase D was synthesized from a 2:1 mixture of  $\text{SiO}_2 + \text{Mg}(\text{OH})_2$  sealed in a welded platinum capsule at 20 GPa and  $\sim 1000^\circ\text{C}$  for about 3 h in a multi-anvil apparatus at Tohoku University. The sample was examined by X-ray powder diffraction and confirmed to be pure phase D. The lattice parameters are:  $a = 4.756(3)\text{\AA}$  and  $c = 4.345(4)\text{\AA}$ . These values are similar to earlier reports (Ohtani et al., 1997; Yang et al., 1997) from samples whose chemical com-

position ranged from  $\text{Mg}_{1.11}\text{Si}_{1.89}\text{H}_{2.22}\text{O}_6$  (Yang et al., 1997) to  $\text{Mg}_{1.84}\text{Si}_{1.73}\text{H}_{2.81}\text{O}_6$  (Ohtani et al., 1997). Phase E was obtained from the same batch used for a previous X-ray diffraction study (Shieh et al., 2000a). It was synthesized in a Walker-type multi-anvil press at the Geophysical Laboratory of the Carnegie Institution of Washington using a 1:2 mixture of  $\text{SiO}_2 + \text{Mg}(\text{OH})_2$  compressed to 14.5 GPa and heated to  $1000^\circ\text{C}$ . The chemical composition determined by electron probe microanalysis is  $\text{Mg}_{2.23}\text{Si}_{1.18}\text{H}_{2.80}\text{O}_6$  and the lattice parameters are:  $a = 2.9653(5)\text{\AA}$  and  $c = 13.890(4)\text{\AA}$  (Shieh et al., 2000a).

Phases D and E samples were first examined by infrared spectroscopy at ambient conditions by placing powdered samples on top of a diamond anvil (D and E) or a KBr substrate (D). Further measurements were then performed at high pressures in a diamond anvil cell. The high-pressure cells used natural type IIa diamonds with 400- $\mu\text{m}$  diameter culets. The samples were prepared by crushing the small single crystals into polycrystalline foils on diamond anvils without further grinding. The foils were loaded into a  $\sim 100\text{-}\mu\text{m}$  diameter gasket hole such that they filled less than 50% of the sample chamber volume and were confined entirely within one-half of the hole. This arrangement allowed background measurements to be performed from the other side of the hole without contamination from the sample. KBr powder, serving as a pressure medium, was used to fill the empty part of the sample chamber and to cover the sample. Small ruby balls were placed near the center and edge of the sample chamber for pressure determination (Mao et al., 1978).

High-pressure infrared (IR) spectra were collected at beamline U2A of the National Synchrotron Light Source. The synchrotron IR beam was focused by a nitrogen gas purged microscope (Bruker IRscope II) and a  $30\text{ }\mu\text{m} \times 40\text{ }\mu\text{m}$  aperture was used during the experiment. Experiments were performed solely in transmission mode and the mid-IR ( $400\text{--}4000\text{ cm}^{-1}$ ) signal was collected using a Bruker IFS 66v/S FTIR spectrometer and a liquid nitrogen-cooled MCT detector with a resolution of  $4\text{ cm}^{-1}$ , which corresponds to an uncertainty of  $0.015\text{ \AA}$  near  $3600\text{ cm}^{-1}$ . At each pressure, the final IR absorption spectrum was obtained by subtracting the background spectrum from the sample spectrum. Pressures were measured before and after each IR measurement, and the pressure difference was generally less than 1 GPa. The pressures measured from ruby positions near the center and edge showed differences of  $\sim 0.5$  GPa at 13 GPa,  $\sim 1$  GPa at 25 GPa and  $\sim 2$  GPa at 40 GPa. Only the pressures recorded after IR measurements are reported in this study. Special care was taken to avoid the contamination of our IR measurements by ruby grains. Data processing was carried out using the Peakfit program and the spectral data were fitted to a combined Gaussian–Lorentzian profile function.

## 3. Results

### 3.1. Phase D

The infrared spectrum of phase D measured at ambient conditions showed 13 observable modes (Fig. 1). To clarify potential ambiguity arising from the contamination by diamond at  $2000\text{--}2500\text{ cm}^{-1}$ , phase D samples were examined on diamond and KBr substrates. The peak at  $1604\text{ cm}^{-1}$  was assigned as the H–O–H-bending vibrational mode. The peaks at  $2102$  and  $2240\text{ cm}^{-1}$  may be strong H bonds of phase D but they were obscured at high pressures by interference with diamond. Ten modes attributable to phase D at elevated pressures were found in this study (Table 1). There are four modes between  $656$  and  $836\text{ cm}^{-1}$  as well as modes at  $1044$  and  $1217\text{ cm}^{-1}$ . At frequencies below  $2000\text{ cm}^{-1}$ , the Raman spectrum of phase D shows a broadly similar pattern that features a group of peaks in the  $600\text{--}800\text{ cm}^{-1}$  region with additional modes at  $1078$  and  $1269\text{ cm}^{-1}$  (Frost and Fei, 1998; Xue et al., 2008). Possi-

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