RAMAN AND INFRARED SPECTRA OF PHASE E, 
A PLAUSIBLE HYDROUS PHASE IN THE MANTLE

TERRENCE P. MERNAGH

Australian Geological Survey Organisation, GPO Box 378, Canberra, ACT, 2601, Australia

LIN-GUN LIU

Institute of Earth Sciences, Academia Sinica, Taipei, Taiwan 115

ABSTRACT

Micro-Raman and micro-infrared spectra of the silicate and principal OH-stretching regions have been obtained from a well-characterized crystal of phase E (Mg$_{2.17}$Si$_{1.61}$H$_{3.62}$O$_6$) containing approximately 18 wt.% H$_2$O. The number of observed infrared and Raman bands exceeds the number predicted by factor-group analysis for a crystal of phase E with space group $R3m$. This finding suggests that some long-range order may exist in phase E, or that it possesses a superstructure that lowers the overall symmetry of the crystal. Although phase E contains layers of brucite-type units linked by SiO$_4$ tetrahedra and MgO$_6$ octahedra, the lower frequencies and the broadness of the OH-stretching bands of phase E (in comparison to brucite) indicate that the hydrogen bonding is stronger than that in brucite. There is a close similarity between the Raman spectra of phase E and forsterite below 1000 cm$^{-1}$. This may be explained by assuming that the vibrations of the isolated SiO$_4$ tetrahedra dominate the Raman spectrum of phase E below 1000 cm$^{-1}$. Tentative assignments of the observed bands are made by comparison with computed spectral modes and the corresponding spectra of brucite and forsterite.

Keywords: hydrous magnesium silicate, phase E, micro-Fourier-transform infrared spectroscopy, micro-Raman spectroscopy, mantle.

INTRODUCTION

There is currently considerable interest in the state of hydration of the mantle. Liu (1987) has estimated that the Earth’s mantle might contain more than five times the present content of H$_2$O in the hydrosphere and crust. In order to hold this amount of H$_2$O inside the Earth, there must be some magnesium silicates that can accommodate it and that are stable at appropriate pressures and temperatures. In addition to the three hydrous magnesium silicates (phases A, B and C), synthesized by Ringwood & Major (1967), there are several other dense hydrous magnesium silicates (e.g., phase D: Liu 1987).

$^1$ E-mail address: terry.mernagh@agso.gov.au
Phase E was first reported by Kanzaki (1989, 1991) as part of a study of phase equilibria of hydrous materials at pressures above 120 kbar. Phase E is generally formed in the range 130–155 kbar and 1000–1200°C, and hence, may be stable at depths ranging from the lower regions of the upper mantle to the transition zone.

X-ray- and electron-diffraction studies (Kudoh et al. 1993) showed that phase E has a cation-disordered structure with a rhombohedral arrangement of layers of brucite-type units. The layers are cross-linked by silicon in tetrahedral coordination, magnesium in octahedral coordination, and hydrogen bonds. Interlayer octahedra share edges with intralayer octahedra. Interlayer tetrahedra would be expected to share faces with intralayer octahedra, but to avoid this, there are vacancies within the layers. Kudoh et al. (1993) suggested that there is no long-range order in phase E, Mg and Si being distributed statistically throughout an essentially close-packed arrangement of oxygen atoms.

The Raman-active OH-stretching bands of phase E were recently reported by Ohtani et al. (1995) and the first complete Raman spectrum of phase E was published by Liu et al. (1997). In this paper, we examine the Raman spectrum of phase E in more detail and compare it to the corresponding infrared spectrum of the same sample.

**EXPERIMENTAL**

Single crystals of phase E (~100 µm diameter) were synthesized at 155 kbar and 1200°C for 22 minutes by Inoue et al. (1995) and at 150 kbar and 1000°C for 3 hours in the present study. The crystal structure of samples synthesized in the present study was confirmed by a micro-focus X-ray diffractometer. Electron-microprobe analysis of the samples synthesized in the present study gave Mg/Si = 1.90 ± 0.02, and the amount of H2O, 18.2 ± 0.9 wt.%, was estimated by difference. The amounts of H2O in two different samples of phase E were estimated to be 15.8 and 18.0 wt.% by Kudoh et al. (1993) on the basis of X-ray-crystal-structure analysis, giving compositions of Mg2.17Si1.62O3.65H3.20O6 and Mg2.18Si1.61H3.62O6, respectively.

Fourier-transform infrared (FTIR) spectra were recorded from 750 to 4000 cm⁻¹ using a Bomen infrared spectrometer and a Spectra-Tech microscope. FTIR spectra were obtained at 4 cm⁻¹ resolution by addition of 500 scans for each sample and reference spectrum. To ensure that only the spectrum of the crystal was obtained, a rectangular region of approximately 30 × 20 µm was selected for analysis by masking the image at an intermediate focal plane within the microscope. Polarized spectra could not be obtained owing to the small size of the crystal used in these studies and the depolarizing effects caused by the microscope objective.

Raman spectra were recorded on a Microdil 28 spectrometer equipped with an Olympus BH2 microscope objective with a focal diameter of 1 µm in diameter on the crystal. A complete description of the Raman instrumentation is given in Liu & Mernagh (1990). Spectra were recorded at approximately 3 cm⁻¹ resolution from 150 to 3800 cm⁻¹ using 514.5 nm excitation and 40 mW power at the sample. All spectra were obtained after 15 accumulations using a 15-s integration time. Raman peaks are accurate to ±1 cm⁻¹, except for the broader OH bands, which are accurate to ±5 cm⁻¹.

**RESULTS AND DISCUSSION**

**Predicted vibrational spectra for phase E**

The X-ray- and electron-diffraction studies of Kudoh et al. (1993) indicate that phase E has a hexagonal unit-cell with space group R3m. However, in order to develop a plausible crystal-structure, Kudoh et al. (1993) proposed that occupied Si tetrahedra cannot share faces with occupied intralayer Mg octahedra. Therefore, all three cation positions (Mg1, Mg2 and Si) are only partly occupied. The pattern of vacancies and interlayer cations is ordered locally, but has no long-range order. In order to simplify the modeling, only the short-range structure will currently be considered, and hence, a factor-group analysis based on the R3m space group predicts the following irreducible representation for phase E:

\[ \Gamma = 3 \, A_{1g} + 3 \, E_u + 4 \, A_{2u} + 4 \, E_u \]

Thus, a total of 14 vibrational modes are predicted for this structure. Owing to the centrosymmetry of the space group R3m, the mutual exclusion rule for normal vibrations in a crystal requires that the u-modes be active in the infrared spectrum and the g-modes be active in the Raman spectrum only.

In order to make band assignments for the observed infrared and Raman spectra of phase E, the VIBRATZ program, a new version of the modeling software by Dowty (1987a), was used to calculate the vibrational frequencies of phase E and to refine the data based on the observed infrared and Raman spectra. The VIBRATZ program requires, as input, the unit-cell parameters and space group, the location of one atom of each equivalent set, obtained from Table 1 in Kudoh et al. (1993), the atomic coordinates of the general equipoint, and a set of force constants that apply to conventional two-atom bonds, three-atom angles, four-atom torsion or bond-plane angles, and interactions of bonds and three-atom angles.

The initial force constants for the Si–O and Mg–O bonds were obtained from Table 2 of Dowty (1987b), and the O–H force constant was obtained from Table 8–1 in Wilson et al. (1980). The bond lengths of Kudoh et al. (1993) were used in these calculations. As Kudoh et al. (1993) could not determine the length of the O–H bond in their X-ray studies, the bond length of O–H in brucite (0.96 Å), determined by neutron-diffraction...
TABLE I. A COMPARISON OF CALCULATED AND OBSERVED VIBRATIONAL FREQUENCIES FOR PHASE E

<table>
<thead>
<tr>
<th>Calculated Frequencies (cm⁻¹)</th>
<th>Observed Frequencies (cm⁻¹)</th>
<th>Mode Assignments</th>
<th>Calculated Frequencies (cm⁻¹)</th>
<th>Observed Frequencies (cm⁻¹)</th>
<th>Mode Assignments</th>
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<td>3642</td>
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<td>Σ₈</td>
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<td>Σ₈</td>
<td>221</td>
<td>221</td>
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</tbody>
</table>

Note that the number of observed bands exceeds the number predicted from the above factor-group analysis, and that some Raman bands seem to coincide with observed and predicted infrared modes. This observation suggests that some long-range order may exist in phase E, or that it has a superstructure that lowers the overall symmetry of the crystal, resulting in an increase in the number of vibrational bands in the spectra. These results conflict with the selected-area electron diffraction (SAED) patterns obtained by Kudoh et al. (1993), which indicate that phase E does not possess any long-range superstructure. However, their interpretation was based solely on the similarities between the diffuse scattering in the SAED and that observed in short-range-ordered alloys. Some possible reasons for the additional bands and tentative assignments are given below.

Micro-FTIR spectrum

The micro-FTIR spectrum of phase E is shown in Figure 1, and the observed frequencies are listed in Table 2. Two strong Si–O stretching bands are observed at 819 and 955 cm⁻¹, with a slight shoulder at 888 cm⁻¹. The two bands at 1439 and 1575 cm⁻¹ occur outside the range of normal Si–O vibrations, and are probably overtones or combination bands. The features in the spectrum between 2330 and 2360 cm⁻¹ are due to a slight decrease in the concentration of CO₂ between the recording of the background and sample spectra, and other weak features below 3000 cm⁻¹ may be overtones or combination bands.
TABLE 2. THE OBSERVED INFRARED AND RAMAN BANDS* OF PHASE E AND FORSTERITE

<table>
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<tr>
<th>FTIR</th>
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<th>Infrared</th>
<th>Raman</th>
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<td>$\delta_{OH}$</td>
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<td>424</td>
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<td>949</td>
<td>957</td>
<td>963</td>
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</table>

$* \text{All frequencies are quoted in cm}^{-1}. \text{ a. This study. b. Selected infrared frequencies of forsterite from Lisie (1975). c. Selected Raman frequencies of forsterite from Chopelas (1991).}$

The two very broad bands at 3368 and 3642 cm$^{-1}$ in the principal OH-stretching region of Figure 1 indicate that either H$_2$O or weakly bonded OH, or both, are present in phase E. This proposal is in accord with the results of the electron-microprobe analysis, which indicate that up to 18 wt.% H$_2$O may be present in phase E. Despite the fact that phase E contains brucite-like layers, all the OH-stretching bands occur at lower frequencies than the relatively sharp OH-stretching band of brucite at 3695–3698 cm$^{-1}$ (Liese 1975, Table II). Both the lower frequencies and the broadness of the OH-stretching bands indicate that the hydrogen bonding in phase E is stronger than that in brucite.

Figure 2 shows an expanded view of the principal OH-stretching for phase E. An approximate value of 100 L mol$^{-1}$ cm$^{-1}$ may be used for the absorptivity of the fundamental OH-stretching vibration in minerals (Rossman 1988) in order to estimate the OH content. An average (2.83 g cm$^{-3}$) of the densities for phase E given in Kudoh et al. (1993) was used in these calculations. Thus by integrating the OH-stretching bands in the infrared spectrum of Figure 2 and using an estimated thickness of 100 $\mu$m, the calculated concentration of OH is 20% by weight. Considering the assumptions made in these calculations, this result is in good agreement with the results of the electron-microprobe analysis (H$_2$O calculated by difference) mentioned above.

**Micro-Raman spectrum**

The complete Raman spectrum of phase E is shown in Figure 3. Note that the three bands between 1000 and 3000 cm$^{-1}$ are due to remnants of a previous carbon coating on the sample, which could not be removed owing to the small size of the crystal. In the principal OH-stretching region, there is one strong band at 3616 cm$^{-1}$.
cm$^{-1}$ and a weak, broad shoulder on the low-frequency side of this band. The profile of the Raman OH-stretching bands is somewhat similar to those of the infrared spectrum (Figs. 1, 2), although the band at lower wavenumbers is not as pronounced in the Raman spectrum. It is worth noting that a new peak was also observed on the high-frequency side of the Raman OH-stretching mode of brucite in the high-pressure study of Duffy et al. (1995). According to these authors, the coinciding bands may be due to mixing of formally infrared and Raman modes due to structural distortion or disorder.

Both the Raman OH-stretching bands of phase E occur at considerably lower wavenumber than the $A_{1g}$ OH-stretching mode for brucite, at 3652 cm$^{-1}$ (Duffy et al. 1995). The higher strength of hydrogen bonding in phase E is shown by the shift to lower wavenumber and by the greater width of the bands in the ambient Raman spectrum. Although phase E is reported to contain layers of brucite-type units (Kudoh et al. 1993), the Raman spectrum contains several intense bands in the low-frequency region above 800 cm$^{-1}$ that are not observed in the Raman spectrum of brucite (Duffy et al. 1995). However, the weak bands at 288, 432 and 717 cm$^{-1}$ (Fig. 3) may correspond to vibrations of brucite-type units, as they all lie within 8–11 cm$^{-1}$ of the reported Raman-active modes of brucite. The Raman-active vibrations of the brucite-like layers are relatively weak, a common feature of many silicates, e.g., pyroxenes (Mernagh & Hoatson 1997). This is due to the predominantly ionic nature of the MgO$_6$ octahedra (Farmer 1974).

It is interesting to note, however, the close similarity of the Raman spectra of phase E and forsterite below 1000 cm$^{-1}$ (Fig. 4). Comparison of the observed infrared and Raman frequencies of phase E with those of forsterite (Table 2) shows that the Raman bands of phase E occur at slightly lower wavenumber than those of forsterite. A similar relation occurs for the Raman spectra of $\beta$-Mg$_2$SiO$_4$ and the hydrous $\beta$-phase (Mernagh & Liu 1996). Although phase E and forsterite have quite different structures, they both contain individual SiO$_4$ tetrahedra. Thus, it seems that the vibrations of SiO$_4$ tetrahedra dominate the Raman spectrum of phase E below 1000 cm$^{-1}$.

The inference that many of the observed Raman modes (particularly those between 800 and 1100 cm$^{-1}$) are due to SiO$_4$ vibrations is supported by the results of Paques-Ledent & Tarte (1973) on forsterite containing varying $^{28}$Si/$^{30}$Si and $^{24}$Mg/$^{26}$Mg ratios. They found that bands in the range 800–1100 cm$^{-1}$ are not affected by the proportion of Mg-isotopes, indicating that little or no Mg translations are involved in these high-frequency modes. However, the bands between 991 and 885 cm$^{-1}$ are sensitive to variations in the proportions of Si-isotopes, and they inferred that these bands are related to the $v_3$ anti-symmetric stretching of the SiO$_4$ tetrahedra, in which significant Si displacement is expected. They showed that there was significant mixing of $v_1$ and

![Micro-Raman Spectrum of Phase E](image)

**Fig. 3.** Micro-Raman spectrum in the region 100 to 3800 cm$^{-1}$ recorded from a single crystal of phase E. Note that the bands between 1000 and 3000 cm$^{-1}$ are due to remnants of a carbon coating on the sample from previous studies (see text for further explanation).
\( \nu_3 \) character for the intense bands at 856 and 824 cm\(^{-1}\). Paques-Ledent & Tarte (1973) also found that infrared bands at 466, 425, 415, 364, 320, 300 and 277 cm\(^{-1}\) show large shifts in frequency with Mg-isotope variations, but only small shifts with Si-isotope variations. They inferred that these bands are associated with large translations of Mg atoms and also possibly SiO\(_4\) rotations. All the remaining bands in their experiments seem to involve displacements of both Mg and Si. Therefore, the assignments in Table 2 are based on similar assignments for forsterite as reported by Chopelas (1991).

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**References**


![Fig. 4. Comparison of the micro-Raman spectrum in the region 100 to 1020 cm\(^{-1}\) for forsterite (top) and phase E (bottom).]
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