

In situ high pressure IR spectroscopic observations on the upper mantle anhydrous minerals using diamond anvil cell

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Most nominally anhydrous minerals (NAMs) in the Earth's upper mantle can contain small amounts of hydrogen (i.e. "water"), structurally bond as hydroxyl. Structurally bounded water causes important influences on many physical properties of mantle rocks. The influence seems to be controlled by hydrogen atoms positions in crystal structure. In most of previous researches, hydrogen atoms positions have been estimated by comparison between the theoretically calculated IR spectra and the experimental results, which obtained at ambient pressure [1, 2]. Therefore, the influence of pressure on hydrogen atom positions has not been identified yet. However, the physical properties relating to hydrogen atom (electric conductivity, viscosity and more), have been measured at high pressure conditions. Thus it is important to clarify the influence of pressure on hydrogen atoms positions.

To observe the influence of pressure on IR spectra, high-pressure experiments have been conducted at pressures of 0.4 – 9.0 GPa at room temperature. The experiments were performed with diamond anvil cell by using natural olivine (Ol) and synthetic forsterite (Fo) as starting materials. The pressure medium was KBr powder or fluorinert. Pressure was determined by ruby fluorescence method [3]. The IR spectra were obtained with a vacuum type Fourier transform infrared spectrometer (Jasco: FT-IR6100, IRT5000).

Clear OH stretching vibration bands could be observed for samples with water concentration over ~100 wt.ppm. The non-polarized IR spectrum of synthesized Fo showed four bands; two stronger ones at 3610, 3575 cm⁻¹ and two weaker bands at 3550, 3475 cm⁻¹ at ambient pressure. The band at 3475 cm⁻¹ disappeared in the spectrum of randomly oriented Fo at ≥5.6 GPa. The band at 3610 cm⁻¹ shifted to low wavenumber with increasing pressure. After decompression, the spectrum return to the almost same position and intensity before increasing pressure. Thus it indicates that these bands shift is a reversible change.

The polarized to *a*-axis IR spectrum of natural Ol showed three bands; 3610, 3598 and 3575 cm⁻¹ at ambient pressure. The band at 3610 cm⁻¹ shifted to low wavenumber and became weaker with increasing pressure. The band at 3575 cm⁻¹ shifted to high wavenumber, which results is opposite to the band at 3610 cm⁻¹, and also became weaker with increasing pressure. The polarized to *b*-axis IR spectrum of natural Ol showed two bands; 3598 and 3575 cm⁻¹. The band at 3598 cm⁻¹ did not change with increasing pressure. In this experiment, the diamond anvils touched sample directly above 8 GPa, so we could not observe the spectrum after decompression.

[1] Umemoto et al.: *Am. Min.*, 96, 1475-1479, 219 (2011) [2] Sakurai et al.: *J. Comput. Chem. Jpn.* [3] Mao et al.: *J. Appl. Phys.* 49, 3276-3283 (1978)

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