In-situ observation and Raman spectroscopy of water, ice VI and ice XII under high pressure

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Introduction

H_2O ice has more than fourteen polymorphs and two amorphous phases. Except for ice X, these phases exist at a pressure range lower than a few GPa. Therefore, the phase diagram of H_2O at relatively low-pressure region is complex including two metastable crystalline phases: ice IV (Bridgman 1935 J Chem Phys) and ice XII (Lobban et al., 1998 Nature, Chou et al., 1998). Salzmann et al. (2002 J Phys Chem) identified this phase as ice XII based on diffraction data (Lobban et al., 1998) and as the new ice phase based on Raman spectroscopy (Chou et al., 1998).

Raman spectra of water

At 1 degree C, we obtained Raman spectra of water before its crystallization. A kink in the pressure dependence of Raman frequencies can be seen at around 0.4 GPa. Such changes are also observed in the distribution of peak area and the full width at the half height (FWHH). This change is similar to the changes observed at 25, 100 and 300 degree C (Kawamoto et al., 2004 J Chem Phys). Any sign of structure change was not detected through in-situ visual observation cross a possible boundary. Nature of this structural behaviour from sparse water to dense water remains uncertain.

Raman spectra of ice VI

Raman spectra of ice VI was obtained at 1, 13 and 25 C as a function of pressure. We found the similarity in the Raman frequency between those of ice VI and the lower two peaks of water. The highest peak of water can be from free molecules, and the ice phases have no such free molecule. The pressure dependences of Raman frequencies between those of dense water and ice VI are consistent with similar structure of water and ice VI. Under atmospheric pressure, the water is known to have a cage-type hexamer (Liu et al., 1996 Nature), which is a structural unit of ice VI. We also compare the Raman frequencies of water and ice VII obtained at 300 degree C (Kawamoto et al., 2004 J Chem Phys), and we will discuss about this relationship in our presentation.

Raman spectra of ice XII

During determining the melting curve of ice VI, we happened to find this phase, ice XII. The present ice XII is characterized by the identical melting curve to the new phase reported by Chou et al. (1998) and has a euhedral shape, which is different from the rounded shape of the new phase by Chou et al. (1998). The obtained Raman spectra are similar to ice VI but their peak separation indicates that this phase is different from ice VI and similar to new ice or ice XII. The obtained low frequency data are not quite well assigned in our spectrometer, but still consistent with the presence of the 193 cm ˆ-1 peak reported for the new ice phase (Chou et al., 1998) and ice XII (Salzmann et al., 2002).

Ice XII is formed from water by compression and also by slow decompression of ice VI. We did not see the rounded shape ice XII during the crystallization from water. However, melting of ice XII seems much more sluggish than melting of ice VI to water, and during its melting the crystalline shape of ice XII is naturally rounded. The change from ice XII to ice VI was not visually detected during our experiments. Ice XII looks to exist in a narrow pressure range. Transition between ice XII and VI remains to be investigated in order to understand about metastable phase processes.

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