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Stabilizing of methane hydrate and transition to a new high-pressure structure at 40 GPa

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ABSTRACT

High-pressure experiments of methane hydrate with a composition of full-occupancy of structure I were performed in a pressure range from 0.2 to 86 GPa. X-ray diffractometry and Raman spectroscopy revealed that methane hydrate transformed from a known high-pressure structure, filled-ice-Ih structure, to a new high-pressure structure at approximately 40 GPa. The reason for the outstanding retention of the filled-ice-Ih structure up to 40 GPa was examined, because the filled-ice-Ih structures for other gas hydrates decompose below 6.5 GPa. In the Raman spectra, new intramolecular vibration modes softer than the original ones appeared at 14 to 17 GPa, indicating that additional intermolecular interaction arose around the methane molecules. The additional interaction might be induced by symmetrization of the hydrogen bonds forming the framework. The symmetrization of the framework and the subsequent additional interactions between the methane molecules and the framework water molecules and also between the methane molecules are likely the cause of the excellent stabilization. The new high-pressure structure survived at least to 86 GPa.

Keywords: Methane hydrate, high-pressure study, phase transition, Raman spectroscopy, XRD data, crystal structure