Intramolecular interactions in hydrogen hydrate and its implication for their stabilities under high pressure

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Filled ice structures of hydrogen hydrates, filled ice II and filled ice Ic, are formed under high pressure at room temperature. The filled ice II structure was synthesized at around 0.8 GPa, and the filled ice II structure transformed to the filled ice Ic structure at 2.3 GPa. This filled ice Ic structure was maintained to 60 GPa at room temperature and symmetrization of the hydrogen bond in the framework of water molecules was predicted to occur. The filled ice Ic structure shows the outstanding stability under high pressure. Therefore, it is expected that the filled ice Ic structure possess intermolecular interactions which enable stability. However, the reasons for the structural changes of the filled ice structure and the stability under high pressure have not yet been explained. In this study, the phase change of the filled ice structures of hydrogen hydrate was clarified and the reasons for the remarkably stabilized filled ice structures with regard to the intermolecular interactions were examined.

A lever-and-spring type diamond anvil cell was used in the high-pressure experiments. The pressure was measured by ruby and Sm:YAG fluorescence methods. In situ optical microscopy, X-ray diffractometry and Raman spectroscopy were performed to characterize the samples.

The suppress of the rotation of hydrogen molecules in hydrogen hydrate and partly extracting of hydrogen molecules were observed at 15 to 20 GPa. In addition, symmetrization of the hydrogen bond in the framework of water molecules also occurred at around 35 GPa. At around 60 GPa, the filled ice Ic structure phase transformed to a new high-pressure phase which was maintained at least up to 72 GPa. As for methane hydrate, we showed that an orientational ordering of the guest methane molecules occurred at around 20 GPa Both the orientational ordering of methane molecules in methane hydrate and the extraction of hydrogen molecules in hydrogen hydrate at 15 to 20 GPa might occur in order to moderate unfavorable states caused by the close arrangement, leading to attractive intermolecular interactions between the guest molecules and framework water molecules and between neighboring guest molecules. These interactions might result in the remarkable stability of the filled ice structures both for methane hydrate and hydrogen hydrate. Furthermore, symmetrization of the hydrogen bond indicates that the framework of the structure changes their properties to ionic structure and that the frameworks of the structures themselves become stiffer. Thus, another interaction between the guest molecules and the frameworks are produced. These frameworks and intermolecular interactions were considered to contribute to the additional stability of the filled ice structures.