

高圧氷VI及びVIIへのNaCl固溶の可能性 Incorporation of NaCl into ice VI and ice VII under high pressure.

平井 寿子^{1*}; 山下 福憲¹; 香川 慎伍¹; 門林 宏和¹; 大石 泰生²; 山本 佳孝³

HIRAI, Hisako^{1*}; YAMASHITA, Fukunori¹; KAGAWA, Shingo¹; KADOBAYASHI, Hirokazu¹; OHISHI, Yasuo²; YAMAMOTO, Yoshitaka³

¹ 愛媛大学地球深部ダイナミクス研究センター, ² 高輝度科学研究所, ³ 産業総合技術研究所メタンハイドレート研究センター

¹Geodynamics Research Center, Ehime University, ²JASRI, ³AIST

Icy satellites have been thought to contain a large amount of salts besides water ices. Ice exhibits a wide variety of forms consisting of hydrogen-bonded water molecules. More than sixteen stable and metastable forms have been reported so far. Liquid water can dissolve various kinds of solutes. Whereas, in the previous idea, when water crystallizes, the dissolved solutes are excluded, which results in formation of pure water ices. Recently, Frank et al. [1] and Komatsu et al. [2] reported that NaCl or other salts was incorporated into ice VI and/or ice VII. In these studies, however, it has been still unclear which ice can incorporate NaCl, and amount of salts incorporated and states of the salt in the ice structure have not yet been clarified. In this study, in order to understand possible incorporation of salts in to ice VI and VII structures, high-pressure experiments were performed with a system of H₂O-NaCl, a typical salt, at room temperature.

Lever-and-spring type diamond anvil cell was used. Pressure range examined was from 0.2 to 10 GPa. NaCl aqueous solutions with three concentrations, 1.5, 2.5, and 5.0 w%, were prepared as starting samples. Characterization was made by optical microscopy, X-ray diffractometry (XRD), and Raman spectroscopy.

Similar phase changes were observed for the samples with three different concentrations. The NaCl aqueous solutions finally crystallized to form ice VI above 1.6 GPa, although in case of pure water ice VI is formed at 1.0 GPa at room temperature. At the pressure range from 2.1 to 3.2 GPa, a new high-pressure phase, of which diffraction pattern was not explained by ice VI, ice VII, and solid NaCl, was observed. Above 3.2 GPa, ice VII and solid NaCl appeared. The high-pressure phase observed may correspond to a phase having a modified structure of NaCl-dihydrate reported by Nakayama et al. [3]. Unit cell volumes of ice VII calculated expanded larger than those of pure ice VII. The result was opposite sense to those by Frank et al, where the volumes decreased smaller than those of pure ice VII. The amounts of the volume expansion for 2.5 and 5.0 w% samples were larger than those of 1.5 w% samples. The volume expansions of the former two samples were almost similar. The results suggested that limitation of incorporation into ice VII is less than 2.5 w%. The O-H vibrational modes shifted to higher frequencies by 10 to 20 cm⁻¹ and 5 to 10 cm⁻¹ from those of pure ices for ice VI and ice VII, respectively.

All experimental results indicated that NaCl is incorporated both into ice VI and ice VII at room temperature. The amounts of incorporation were estimated to be up to 2.5 w%. Such large amount of incorporation of salt is expected to effect on physical properties of ices, which is important in inferring the interiors of icy bodies.

1. M. R. Frank et al., PEPI 155 (2006) 152; M. R. Frank et al., PEPI 170 (2008) 107; M. R. Frank et al., PEPI 215 (2013) 12.
2. K. Komatsu et al., Abstract of Annual meeting of Jpn. Society High Pressure Tech. (2010).
3. K. Nakayama master thesis (2012).

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