

Pressure-induced changes in hydrogen bonds in hydrous materials

Hiroyuki Kagi^{1,*}, Riko Iizuka¹, Kazuki Komatsu¹, Yu Yamaguchi¹ and Shin-ichi Machida²

¹Graduate School of Science, The University of Tokyo, Tokyo 113-0033, Japan

²Geodynamic Research Center, Ehime University, Ehime 790-8577, Japan

1 Introduction

Water and hydrogen play important roles on dynamics and mineral properties of deep earth and planets. Pressure-induced changes in structure of hydrous materials including hydrous minerals are one of the fundamental research targets to the understanding properties of hydrogen in the deep earth and planets. We report our recent research activities on X-ray diffraction measurements at high pressure conducted at the beamline-18C, Photon Factory.

2 Experimental procedures

We are going to introduce a couple of representative experimental results on $\text{Ca}(\text{OH})_2$ and ice at high pressure using diamond anvil cells. Angular-dispersive synchrotron XRD patterns of the powder samples were obtained at high pressure at the BL-18C, High Energy Accelerator Research Organization (KEK). X-ray diffraction patterns of ices were observed at low temperatures down to 100 K. A monochromatized incident X-ray with energy of 20 or 30 keV (ca. 0.6 or 0.4 Å in wavelength) was used. The beam was collimated to a diameter of 30–60 μm. The diffracted X-ray patterns were recorded on an imaging plate (IP) detector. Profile fitting was conducted using a symmetric pseudo-Voigt function with the software PDIndexer [1].

3 Pressure responses of $\text{Ca}(\text{OH})_2$ and H–D isotope effects on pressure-induced phase transitions [2]

The pressure responses of $\text{Ca}(\text{OH})_2$ and the isotope effect on the phase transition were investigated at room temperature from powder X-ray diffraction and single-crystal Raman and IR spectra using diamond anvil cells under quasi-hydrostatic conditions in a helium pressure-transmitting medium. Phase transformation and subsequent peak broadening (partial amorphization) observed from the Raman and IR spectra of $\text{Ca}(\text{OH})_2$ occurred at lower pressures than those of $\text{Ca}(\text{OD})_2$. In contrast, no isotope effect was found on the volume and axial compressions observed from powder X-ray diffraction patterns. X-ray diffraction lines attributable to the high-pressure phase remained up to 28.5 GPa, suggesting no total amorphization in a helium pressure medium within the examined pressure region. These results suggest that the H–D isotope effect is engendered in the local environment surrounding H(D) atoms. Moreover, the ratio of sample to methanol–ethanol pressure medium (i.e., packing density) in the sample chamber had a significant effect on the increase in the half widths of the diffraction lines, even at pressures below the hydrostatic limit of the pressure medium.

In conclusion, we have confirmed that a reversible pressure-induced phase transition occurs in $\text{Ca}(\text{OH})_2$ at around 6 GPa at room temperature. XRD peaks of the high-P phase were observed even at 28 GPa, whereas all the Raman and IR spectroscopic peaks disappeared at pressures greater than about 20 GPa under quasi-hydrostatic conditions. The H–D isotope effect was observed on the pressures of transformation to the high-P phase and partial amorphization; the transition pressure of $\text{Ca}(\text{OH})_2$ is lower than that of $\text{Ca}(\text{OD})_2$. In contrast, no isotope effect was found on the volume and axial compression of $\text{Ca}(\text{OH})_2$. The present results suggest that the pressure responses accompanying the isotope effect are closely related to hydrogen bond interactions.

4 Uptake of salt components in high-pressure ices [3]

Recently, uptake of salt components, for instance LiCl and NaCl, into ice VII, a high-pressure phase of ice, have been reported (eg., Klotz et al., 2009) in contrast to the incompatible nature of salts into the crystal structure of normal ice (ice Ih).

We have determined precisely the lattice volumes of high-pressure phases of ices (see Fig. 1 for the P-T conditions). The obtained experimental results showed several percents of volume excess in ice VII which was grown from MgCl solution. The results suggest that substantial amount of MgCl_2 was contained in ice VII. The result is the first report on the uptake of divalent metal ion salt into a high-pressure phase of ice. The details will be reported in an original paper in preparation.

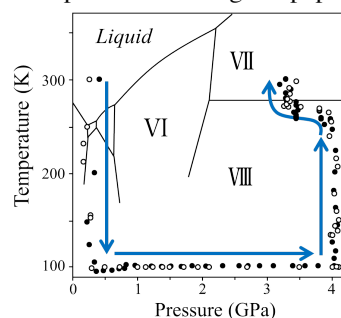


Fig. 1 *P-T* path of experiments on the phase diagram of H_2O .

References

- [1] Y. Seto et al. Rev. High Press. Science Tech., 20 (2010) 269.
 - [2] R. Iizuka et al. Physics and Chemistry of Minerals, 38 (2012) 777.
 - [3] Y. Yamaguchi et al., (to be submitted).
- * kagi@eqchems.s.u-tokyo.ac.jp