In situ observation of the pressure-induced phase transition in calcium hydroxide, portlandite

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Hydroxides, $M(OH)_2$, of divalent metals with the CdI2 structure (trigonal) are interesting model systems for the investigation of the high-pressure behavior of hydrogen bonding in solids. Powder sample of portlandite, $Ca(OH)_2$, exhibits a reversible pressure-induced amorphization at 11 GPa and the c-axis is initially much more compressible than the a-axis. In contrast, single crystal of portlandite undergoes a transition to a high-pressure phase at 6 GPa and room temperature due to the effect of grain size. In addition, it is likely that deviatoric stress from pressure transmitting media is an important factor for a pressure-induced amorphization. The mechanism of high- pressure phase transition of portlandite remains unknown. We investigated the high-pressure behavior of both powder and single crystal portlandite samples under quasi-hydro static conditions. Moreover, the isotope effect on the pressure-induced responses was studied for the purpose of deciphering the phase transition mechanism.

Powder samples of $Ca(OH)_2$ and $Ca(OD)_2$ were synthesized by the reaction of $Ca(NO)_3{\cdot}4H_2O$ and KOH dissolved in $H_2O(D_2O)$. The single crystal is obtained by recrystallizing from the powder sample on the glass plate in a desiccator with silica gel and soda lime. These samples were mounted in clamped DACs with a few small ruby chips. Applied pressure was determined by ruby fluorescence technique and the hydrostaticity was also estimated from the peak width of the ruby fluorescence. As pressure medium, 4:1 methanol-ethanol mixture or He gas were used. Raman spectra of OH and OD stretching vibration modes were measured with the 514.5 nm beam of an Ar ion laser and a CCD detector. Angular-dispersive synchrotron X-ray diffraction experiments up to 25 GPa were performed on the BL-18C beamline in the Photon Factory, KEK.

Notable difference was found in the Raman spectra at 7 GPa between powder and single crystal in the methanol-ethanol. Split peaks were found for powder $Ca(OH)_2$ in the He with increasing pressure. The observed XRD pattern showed unknown peaks before amorphization. Additionally, these unknown peaks were quite different between in methanol-ethanol and He pressure media. These observations suggest that there are several new high-pressure phases, and both hydrostatic condition and grain size may affect on the mechanism of the transitions. No remarkable difference in isotope effect was found in both Raman spectra and the XRD pattern.