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Phase transitions and hydrogen bonding in deuterated calcium hydroxide: High-pressure and high-temperature neutron diffraction measurements

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ABSTRACT

In situ neutron diffraction measurements combined with the pulsed neutron source at the Japan Proton Accelerator Research Complex (J-PARC) were conducted on high-pressure polymorphs of deuterated portlandite ($\text{Ca}(\text{OD})_2$) using a Paris–Edinburgh cell and a multi-anvil press. The atomic positions including hydrogen for the unquenchable high-pressure phase at room temperature (phase II') were first clarified. The bent hydrogen bonds under high pressure were consistent with results from Raman spectroscopy. The structure of the high-pressure and high-temperature phase (Phase II) was concordant with that observed previously by another group for a recovered sample. The observations elucidate the phase transition mechanism among the polymorphs, which involves the sliding of CaO polyhedral layers, position modulations of Ca atoms, and recombination of Ca–O bonds accompanied by the reorientation of hydrogen to form more stable hydrogen bonds.

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1. Introduction

Hydroxides of a divalent metal $M(\text{OH})_2$ ($M = \text{Mg}, \text{Ca}, \text{Mn}, \text{Co}, \text{Ni}, \text{Cd}, \text{etc.}$) under ambient conditions assume a brucite-type layered hydroxide with a CdI_2 structure (trigonal, space group $P\bar{3}m1$). The structure consists of MO_6 octahedral layers with hydrogen bonds between the layers. Hydrogen-bearing materials with this simple structure show complicated pressure and/or temperature responses, which have been of interest in various fields since the 1990s. The changes of structure and properties related to the hydrogen bonding interactions depend upon the size of the divalent metal cations. The pressure responses of different divalent metal hydroxides have been investigated using various methods such as optical spectroscopy, X-ray diffraction, neutron diffraction, and numerical simulations. Diverse behaviors have been observed at high pressure: high stability of the starting structure over a

wide pressure range [1], pressure-induced amorphization [2–4], phase transitions [5–8], repulsion between hydrogen atoms within interlayers [9,10], and partial amorphization of the H sublattice [11,12]. Proton disorder at high pressure has also been predicted from theoretical simulations [13]. Pressure-induced changes in hydrogen bonding are of particular importance not only in material physics and crystallography but also in geoscience, because $M(\text{OH})_2$ is one of the simplest model structures of the hydrous minerals that exist in subduction zones and transport water from the Earth's surface to the deep mantle.

Calcium hydroxide ($\text{Ca}(\text{OH})_2$) as portlandite (hereafter phase I, named following the usage of Leinenweber et al. [14]) shows a variety of phase transitions with changing pressure and temperature. These phase transitions are unique among the brucite-type $M(\text{OH})_2$ hydroxides, likely due to the large ionic radius of the Ca. Phase I can assume two high-pressure phases depending on the P – T conditions: at room temperature phase II' forms at 6–8 GPa [5–8]; the other phase (hereafter phase II, named following the usage of Leinenweber et al. [14]) emerges at > 6–7 GPa and high temperature > 200 °C [14–16]. Neutron diffraction is useful for the study of changes in the crystal structures of hydrogen bearing materials and for the identification of their phase transition mechanisms, including the behavior of

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hydrogen bonding. (Hydrogen positions cannot be easily determined by X-ray diffraction.) However, there have been few high-pressure neutron diffraction studies of $\text{Ca}(\text{OH})_2$, with no *in situ* neutron diffraction studies of phases II' or II having been reported. This lack of research is presumably due to not only the technical difficulties of high-pressure neutron diffraction but also to other difficulties specific to the characteristics of the sample. The pressure-induced phase transition of portlandite is very sensitive to the hydrostaticity of the applied pressure [5–8]: phase II' is difficult to obtain except under highly hydrostatic conditions. It coexists with phase I over a wide pressure range up to 10 GPa, which impedes the observation of diffraction patterns exclusively from phase II', as we previously reported [7,8]. Furthermore, both phase II' and phase II are normally unquenchable. A previous neutron study by Leinenweber et al. [14] determined the hydrogen positions of phase II, which were recovered to ambient pressure after quenching the sample in liquid N_2 [16], via neutron diffraction measurements at 0.1 MPa and 11 K. However, the structure and hydrogen positions observed after quenching are not certain to be identical to those of the original phase II at high pressure and high temperature. Subsequent *in situ* powder neutron diffraction measurements by Pavese et al. [17] of $\text{Ca}(\text{OH})_2$ (not deuterated) at room temperature and high pressures up to 10.9 GPa using a Paris–Edinburgh (P–E) cell did not observe phase II', likely because the pressure condition was insufficiently hydrostatic due to their use of NaCl powder as a pressure medium. Xu et al. [18,19] reported a neutron diffraction study of the phase I of $\text{Ca}(\text{OD})_2$ at high pressure and high temperature using a toroidal anvil press. They elucidated in detail the behavior of hydrogen bonding at high pressure and/or temperature only in a limited *P–T* stability field up to 4.53 GPa at room temperature and up to 2.1 GPa at $\sim 500^\circ\text{C}$. No report has established *in situ* neutron diffraction measurements for each of phase II' and phase II under pressure.

We recently reported the crystal structure of phase II' and the mechanism of the phase transition from phase I to phase II' by *in situ* X-ray diffraction measurements at high pressure and room temperature [8]. Our previous study, however, did not experimentally determine the hydrogen positions in phase II'. Also important is to specify the high-pressure behavior of hydrogen bonding and the phase relations among phases I, II', and II.

A strong neutron flux is required for *in situ* neutron diffraction measurement to allow the effective determination of the weak signals derived from the tiny sample volumes observed through the small window of the high-pressure device. A new beamline for high-pressure and high-temperature neutron experiments has recently been established at the Japan Proton Accelerator Research Complex (J-PARC). This new beamline is expected to provide significant new information about the pressure responses of hydrogen arrangements at high temperature.

This work reports *in situ* powder neutron diffraction measurements performed to investigate hydrogen positions in the high-pressure phases of $\text{Ca}(\text{OD})_2$. To overcome the previous difficulties described above, a P–E cell with modified anvils (Iizuka et al. [20]) and a multi-anvil press newly designed for neutron diffraction at high pressure and high temperature (Sano et al. [21]) were used. Several technical improvements were applied to achieve more detailed structure analyses, which included the hydrogen positions in portlandite. Raman spectra of phase II' were also obtained to clarify the pressure response of the hydrogen bonds.

2. Experimental methods

2.1. Sample preparation

Powdered $\text{Ca}(\text{OD})_2$ was synthesized by the deuteration of CaO powders (assay minimum 99.9%; Wako Pure Chemical Industries

Ltd.) using D_2O (minimum isotope purity 99.96 atom %D; Aldrich Chemical Co. Inc.). CO_2 and water adsorbed on the CaO powder were degassed by heating at 880°C for one day in a porcelain crucible. The CaO and excess D_2O were then held in a Teflon-lined stainless steel autoclave at 235°C for one week. After the hydrothermal processing, the precipitates were filtered and washed with D_2O . The resulting product was dried at room temperature under vacuum. The synthesized $\text{Ca}(\text{OD})_2$ powder was identified as phase I by powder X-ray diffractometry (30 kV, 15 mA, $\text{CuK}\alpha$, MiniFlex II; Rigaku Corp.) and Raman spectroscopy (details described in our previous work [7,8]).

2.2. Powder neutron diffraction at PLANET beamline, J-PARC

Powder neutron diffraction experiments were performed using the high-pressure neutron diffractometer PLANET, located at the beamline BL11 in the Materials and Life Science Experimental Facility of J-PARC (Tokai, Ibaraki) [22,23]. The diffraction patterns were measured by the time-of-flight (TOF) method. The neutron beam was generated using a Hg target with pulse repetitions every 40 ms (25 Hz). The PLANET beamline incorporated a focusing mirror for incident neutrons [24,25] and two perpendicular detector banks. Each bank had 160 position sensitive detectors filled with ^3He gas. The detector coverage of each bank was $90 \pm 11^\circ$ against the incident beam in the horizontal direction and $0 \pm 35^\circ$ in the vertical direction. Radial collimators were attached in front of the detector banks to reduce background. The resolution was 0.6% in $\Delta d/d$. The accessible *d*-spacing was normally 0.2–4.2 Å and was doubled in a long wavelength setting. The power of the proton beam used during the present study was around 300 kW.

2.2.1. High-pressure experiments at room temperature using a P–E cell

Neutron diffraction patterns of phase II' were obtained at room temperature using a P–E cell (two-column VX4-type, max. load 200 t; [26]) combined with our recently developed wide aperture anvils, which have an accessible angle of $0 \pm 15^\circ$ in the vertical direction along the compression axis [20]. Cup-shaped anvils of Ni-bound WC (sample volume 35 mm^3 , matched to that of the double toroidal anvils) were used. The details are described in Iizuka et al. [20]. To observe single phase II' under highly hydrostatic conditions above 10 GPa, $\text{Ca}(\text{OD})_2$ powder was encapsulated together with a hydrostatic pressure medium in a TiZr gasket. A 4:1 deuterated methanol–ethanol mixture was used as pressure-transmitting medium. Soon after the sample was charged and before the pressure medium was evaporated, a load was applied up to approximately 10 t until the sample chamber was totally sealed in the TiZr gasket, which was reinforced with an Al-alloy outer ring. An applied load of 45 t generating a pressure of 10.5 GPa led to phase II' being exclusively observed without the presence of phase I. Diffraction patterns were measured at 10.5 GPa and 11 GPa. Despite the pressure being higher than the hydrostatic limit of a methanol–ethanol mixture, an alcohol pressure medium is a better and softer pressure medium than solid NaCl: reasonably sharp diffraction peaks under quasi-hydrostatic condition were observed. The press was placed so that the compression axis was parallel to the incident beam. Incident neutrons passed through one of the anvils, and the neutrons scattered toward 90° were observed through the gasket. The press was aligned to the neutron beam by motorized XYZ stages controlled by the results of quick analysis of the diffraction patterns. A hBN incident collimator with an aperture of 3 mm diameter was used, and Cd foils were placed around the anvils to avoid the contamination of scattering from the surroundings. Two separate sets of data were collected for the intensity correction of the TOF data: one for an empty gasket and one for a vanadium pellet in the

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