Structural consideration of phase transitions in Zn(OH)$_2$ under high pressure

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Abstract. Pressure-induced phase transitions of Zn(OH)$_2$ were investigated under hydrostatic condition at room temperature by an in-situ X-ray powder diffraction method and a visible observation method for a single-crystalline specimen. Two phase transitions were observed in the pressure range up to 4GPa. The first transition occurred at 1.1 GPa and it was a quick single crystal – single crystal transition. The high-pressure phase 1 with a tetragonal $\alpha$-cristobalite-related structure was stable up to 2.1GPa. The coordination number of zinc atoms was 4+2. The second phase transition was observed above 2.1GPa. The high-pressure phase 2 was quenchable to ambient condition. The crystal structure has not been determined yet because the X-ray powder diffraction pattern was too broad to be even indexed. Comparison of polymorphs in Zn(OH)$_2$ suggests that the volume per chemical formula of the high-pressure phase 2 is in 40.0 – 44.5 Å$^3$ at 2.1 GPa and room temperature and that the coordination number of zinc atoms in the phase is probably 4+2 or 5.

1. Introduction

There have been many investigations about high-pressure behavior of M(OH)$_2$-type hydroxides as a simple model of popular hydroxides. Most of M(OH)$_2$-type hydroxides have the hexagonal CdI$_2$-type structure involving MO$_6$ octahedrons at ambient condition. In case of cations preferring a tetrahedral site, the hydroxides have another crystal structure at ambient condition. Zn(OH)$_2$ and Be(OH)$_2$ have a peculiar orthorhombic structure, in which ZnO$_4$ tetrahedrons make up a three-dimensional network [1].

Recently, we have discovered a unique pressure-induced phase transition of Zn(OH)$_2$, of which mineral name is wulfingite, under hydrostatic condition at room temperature [2]: the low-pressure phase (LPP) quickly transformed to the high-pressure phase 1 (HPP1) with a large deformation at 1.1 GPa and the pressure-induced transition had a single crystal to single crystal nature. Structural analysis of the single crystal specimen under high pressure showed that the HPP1 had a tetragonal cell and that the crystal structure was similar to that of $\alpha$-cristobalite (SiO$_2$). The phase transition was reversible with a hysteresis of about 0.4 GPa.

Another phase of Zn(OH)$_2$ has been reported by Baneyeva and Popova [3]. The phase was recovered to ambient condition from 11-12 GPa and 400±40°C and it had the CdI$_2$-type structure. We directly observed the CdI$_2$-type phase at 14.2 GPa and 400°C by an in-situ X-ray diffraction method, and reconfirmed the phase was a high-pressure and high-temperature phase (HPHTP) of Zn(OH)$_2$ [4].
Comparing volumes of the HPP1 and the HPHTP at room temperature, we showed the phase relationship in the pressure range between 0.7 GPa and 1.9 GPa, i.e. the HPHTP was denser than the HPP1 and it was a higher pressure phase than the HPP1. However, the high-pressure behavior in the pressure range higher than 2 GPa has not been observed yet.

The aim of the present study is to observe the high-pressure behavior of Zn(OH)\textsubscript{2} under hydrostatic condition by \textit{in-situ} X-ray powder diffraction method using a large-volume press apparatus and by visible observation of a single-crystal specimen using a diamond anvil cell. Our final goal is to discuss the phase transitions of Zn(OH)\textsubscript{2} from the viewpoint of crystal chemistry.

2. Experimental section

Single crystals of Zn(OH)\textsubscript{2} (wulfingite) were synthesized by an aqua-solution method and the orthorhombic cell parameters of the specimen were \(a_0 = 8.471(2)\, \text{Å}, \, b_0 = 5.140(2)\, \text{Å}\) and \(c_0 = 4.903(2)\, \text{Å}\) at ambient condition [2].

\textit{In-situ} X-ray diffraction observation of powdered Zn(OH)\textsubscript{2} under pressure was carried out using the MAX80 system with a DIA-10 type high-pressure device, installed at PF-AR-NE5C in the Institute of Materials Structure Science, High Energy Accelerator Research Organization [5]. Powdered Zn(OH)\textsubscript{2} and NaCl were separately encased in a Teflon capsule together with a 4:1 methanol / ethanol mixture as a hydrostatic pressure-transmitting medium. X-ray powder diffraction patterns were collected by an energy-dispersive type method at \(\theta = 4.497^\circ\). Pressure was calculated from the volume of NaCl based on the Decker scale [6]. An error of pressure determination was estimated to be less than \(\pm 0.1\, \text{GPa}\).

High-pressure behavior of a single-crystalline Zn(OH)\textsubscript{2} was visibly observed using a diamond-anvil cell with anvils of 450 \textmu m culet in the Institute for Solid State Physics, University of Tokyo. A single crystal specimen of about 100 \textmu m size was placed in a 200 \textmu m hole of a 250 \textmu m thick stainless steel gasket. Small amount of silicon grease was used to prevent the sample to move around and a 4:1 methanol / ethanol mixture was filled in the pressure chamber as a hydrostatic pressure-transmitting medium. Pressure was determined by the ruby fluorescence line from a 5\textmu m size ruby ball placed in the pressure chamber [7].

3. Results and Discussion

3.1. \textit{In-situ} X-ray observation

Typical X-ray powder diffraction patterns of Zn(OH)\textsubscript{2} are shown in figure 1. Two high-pressure phases were observed in the pressure range up to 4 GPa.

The low-pressure phase (LPP) with the orthorhombic cell was stable up to 1.1 GPa, where a sudden change was observed in an X-ray diffraction pattern. The X-ray diffraction pattern collected at 1.9 GPa could be explained as the high-pressure phase 1 (HPP1), of which crystal structure was related to the tetragonal \(\alpha\)-cristobalite structure (space group; \(P4_12_2\) or \(P4_32_12\)) [2]. It was worth while to notice that the diffraction lines of the HPP1 were as sharp as those of the LPP at 0.1 MPa. The high-pressure behaviour of the HPP1 up to 1.9 GPa was consistent with that in our previous investigation [2].

Another pressure-induced phase transition was observed: new broad diffraction lines appeared in X-ray diffraction patterns of the HPP1 above 2.1 GPa. Relative intensities of the new diffraction lines became stronger and stronger by increasing pressure. The diffraction lines of the HPP1 almost vanished at 3.4 GPa. The crystal structure of the HPP2 has not been determined yet because the X-ray powder diffraction pattern collected at 3.4 GPa was too broad to be even indexed. The HPP2 remained in the decompression process and the HPP2 was quenchable to ambient condition, i.e. the phase transition to the HPP2 was irreversible under hydrostatic condition at room temperature.

High-pressure behavior of the HPP2 is remarkably different from that of the HPP1 in two points, as follows: one is that the X-ray diffraction pattern of the HPP was very broad in contrast to that of the HPP1, and the other is that the HPP2 was quenchable to ambient condition while the HPP1 was unquenchable [2].
3.2. Visible observation

Two drastic changes in the shape of a single-crystalline specimen under hydrostatic condition are summarized in figure 2. The phenomena just corresponded to the results of X-ray powder diffraction observation, as shown in figure 1.

No change in shape of the LPP was observed up to 1.0 GPa. A sudden change of the shape of crystal occurred at 1.2 GPa. It should be noted that the specimen remained a single crystal after it transformed into the HPP1. Thus, the LPP-HPP1 transition has a single-crystal to single-crystal nature, although it is accompanied with a large change in shape and volume. The sudden transition indicates that the transition occurs by a displacive mechanism without long-range atomic diffusions proposed in our previous study [2].

The single-crystalline specimen of the HPP1 changed into a lump of grains with many cracks in the compression process from 1.9 GPa to 2.6 GPa. The result indicated that the single crystal of the HPP1 broke down to polycrystals of the HPP2. No remarkable change in the specimen was observed in the decompression process to ambient condition. The result was consistent with the X-ray diffraction observation; the HPP2 remained at ambient condition.

3.3. Crystal structure of HPP2

As above mentioned, the crystal structure of the HPP2 has not been determined yet. So, we consider the crystal structure on the basis of the high-pressure behaviours and crystal structures of the LPP, the HPP1 and the high-pressure and high-temperature phase (HPHTP) with the hexagonal CdI2-type structure [4], assuming that the HPP2 is thermodynamically an intermediate phase between the HPP1 and the HPHTP at 2.1 GPa and room temperature.

Figure 3 shows compression data of the LPP, HPP1 and HPHTP at room temperature. As can be seen from figure 3, the volume per chemical formula of the HPP2 at 2.1 GPa and room temperature is estimated to be in 40.0 Å³ – 44.5 Å³.
Crystal structures of the orthorhombic LPP, the tetragonal HPP1 and the hexagonal HPHTP are illustrated in figure 4. Coordination numbers (CNs) of zinc atom in the LPP and the HPHTP are simply 4 and 6, respectively. The CN in the HPP1 is 4+2: however the longer Zn-O bond distance is about 1.7 times of shorter one [4]. The CN of the HPP2 is probably 4+2, in view of the fact that the HPP1-HPP2 transition occurs even at room temperature while thermal activation is essential for the phase transition to the HPHTP. Another possibility for the CN of the HPP2 may be 5, which is an intermediate value between 4 of the LPP and 6 of the HPHTP.

4. Conclusion
High-pressure behaviour of Zn(OH)$_2$ at room temperature was investigated up to 4 GPa using both an in-situ X-ray powder diffraction method and a visible observation method for a single-crystal specimen. Two transitions were observed by both methods. The crystal structure of the second high-pressure phase was discussed by referring the crystal structures of polymorphs in Zn(OH)$_2$. The present study also showed an advantage of visible observation in a diamond-anvil cell for high-pressure researches.

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