Modulated structure of hemimorphite associated with pressure–induced phase transition

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In situ high–pressure single-crystal X-ray diffraction experiments on natural hemimorphite, ideally Zn₄[Si₂O₇](OH)₂·H₂O, up to 4.7 GPa were conducted to investigate its pressure response property associated with pressure–induced phase transition. After the phase transition confirmed between 2.46 and 3.01 GPa, pairs of satellite reflections were newly found at certain Bragg reflections. The modulation vector q of the satellites was approximately [0, 1/8.4, 0]. The results of the refinements on the averaged structure indicated that the modulation arose from displacements of atomic sites associated with the mechanism of the phase transition, i.e., the rotation of the secondary building unit (SBU). The lower rotation angle of the SBU (Φ) than the value estimated from the non–modulated structure meant that the high–pressure phase contained anti–phase boundaries (APBs) resulting from the opposite direction of the SBU rotation and that the coherency was held across the APBs. Within the coherent domain, the APB’s intervals were distributed along the b–axis with a mean value of 8.4b ≈ 90 Å, where the displacement of each site η(y) was approximated as the first–harmonic. The distribution of the direction of SBU rotation was initially considered to be inhomogeneous, but the elimination of the APBs had proceeded anisotropically and had been aborted below 3.01 GPa.

Keywords: Single–crystal X–ray diffraction, Pressure–induced phase transition, Structural modulation, Anti–phase boundary, Hemimorphite

INTRODUCTION

Hemimorphite, Zn₄[Si₂O₇](OH)₂·H₂O, is a mineral species that occurs in oxidized Zn ore and produces in the oxidation zone of zinc–sulfide deposits (e.g., Medas et al., 2017). It is classified as sorosilicate, and its crystal structure (space group is Imm2) forms a three–dimensional framework by corner–sharing Zn and Si coordination tetrahedra (Fig. 1a). Within the structure, channels constructed with 6– and 8–membered rings of tetrahedra that are lined up with the c–axis contain water molecules (Ito and West, 1932; Barclay and Cox, 1960; McDonald and Cruickshank, 1967). The characteristic feature of the structure of hemimorphite is the secondary building unit (SBU), which is composed of four–membered rings of ZnO₄ tetrahedra and the Si₂O₇ dimers (Seryotkin and Bakakin, 2011). Half of the hydrogen atoms in the hemimorphite structure are bound to oxygen atoms at the O3 site in the framework, and the other hydrogen atoms are bound to oxygen atoms at the O5 site to form H₂O molecules. These hydrogen atoms are thought to form a network of hydrogen bonds (Hill et al., 1977; Takéuchi et al., 1978).

Variations in temperature and pressure lead to phase changes or structural phase transitions of hemimorphite. Cooper et al. (1981) reported a deformation of channels due to a loss of water molecules induced by a heat reaction in situ high–temperature single–crystal X–ray diffraction (SC–XRD). Libowitzky and Rossman (1997) performed analyses of polarized infrared spectra and measurements of birefringence of hemimorphite under low–temperature and demonstrated a second–order phase transition caused by the ordered arrangement of hydrogen positions in its structure at 98(2) K. Furthermore, based on the results from single–crystal neutron diffraction experiments of hemimorphite at 20 K, Libowitzky et al. (1998) observed a superstructure of hemimorphite due to a doubling of its b– and c–axes (the suggested space group was Abm2). They also considered that within this

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structural change occurring in this low-temperature region, hydrogen atoms would be displaced. In contrast, Seryotkin and Bakakin (2011) reported that a pressure-induced phase transition from Imm2 to Pnn2 was observed at around 2.5 GPa (Fig. 1b) by the SC–XRD method but did not report the formation of a superstructure at this phase transition. Despite an interruption of the hydrogen bonding network that occurred within the Pnn2–structure, there was no deformation of the SBU above the transition point. More information about the compressional behavior of hemimorphite is required to verify the association of hydrogen bonds with this phase transition.

In this study, we conducted in situ high-pressure SC–XRD experiments on natural hemimorphite up to 4.70 GPa using a synchrotron radiation source to elucidate the pressure response of the hemimorphite structure. Consequently, we newly discovered a structural modulation that serves as a different mechanism of pressure-induced phase transition. In this paper, we describe this phenomenon in details.

**EXPERIMENTAL PROCEDURES**

**Samples**

Hemimorphite samples from Yunnan, China, which were aggregates of needle crystals and coexisted with quartz, were used for this study. The chemical composition was measured by a field emission scanning electron microscope (JEOL JSM-7001F) equipped with an energy dispersive X-ray spectroscopy (Oxford, INCA). The averaged chemical composition (20 points) was Zn4.007(12) [(Si1.977(7)P0.016(4))O7](OH)2·H2O. The samples of HY1 (60 × 80 × 70 µm3) and HY2 (80 × 70 × 60 µm3) were selected for SC–XRD experiments under ambient and high-pressure conditions, respectively. Neither twins nor cracks in the samples were observed by the polarized light microscopy or X-ray oscillation photographs.

**High-pressure apparatus**

A Merrill–Bassett type diamond anvil cell (DAC) with an open angle of 90° was used as a pressure apparatus. An SUS301 stainless plate (250 µm thick) with a hole (ϕ = 200 µm) was placed on the culet face (ϕ = 600 µm) as a gasket. The HY2 sample and a fragment of natural ruby for measuring pressure were sealed into the hole, which was filled with a pressure medium (methanol: ethanol = 4:1 mixture). Pressure was calibrated using the fluorescence method (Mao et al., 1986).

**SC–XRD experiments**

All SC–XRD experiments were performed using an auto-
mated vertical-type four-circle diffractometer installed at the beam line BL-10A, (Photon Factory, High-Energy Accelerator Research Organization, Japan). The SC-XRD experiments on HY1 and HY2 were conducted under room pressure (RP) and high-pressure (2.46, 3.01, 3.72, and 4.70 GPa) conditions, respectively. The wavelength of synchrotron X-ray radiation was calibrated by the observed unit cell volume of the ruby standard crystal [Standard Reference Material (SRM1990) of the National Institute of Standards and Technology] at ambient conditions. A wavelength of $\lambda = 0.70124$ Å was applied for the measurements under RP, 2.46 and 3.01 GPa, and a wavelength of $\lambda = 0.70116$ Å was applied for the measurements at 3.72 and 4.70 GPa. The lattice constants were determined by using at least 40 centered reflections with the 2θ range set between 17.7 and 60.4° for all pressure points. XRD intensity datasets under RP, 3.01 and 3.72 GPa were collected via the step scan method with $\omega$-scan as follows: 71 steps with step width $\Delta \omega = 0.01^\circ$; counting time 0.5 s. The XRD intensity datasets for satellite reflections were not collected. The standard reflection was observed at every 100 reflections to check the incident beam and sample conditions. At 2.46 and 3.01 GPa, some of the $h + k + l = 2n + 1$ reflections were measured to check for the phase transition that was reported by Seryotkin and Bakakin (2011). Since satellite reflections were observed near certain Bragg reflections during the measurement of 3.01 GPa, scans along multiple reciprocal vectors (counting time 1 s) were performed to evaluate the modulation vector $q$.

**Structure refinements**

Lorentz and polarization corrections were applied for all collected intensity data. The absorption effects of DAC on intensity data were corrected. For low absorption coefficient with small dimension of the samples ($\mu r \sim 0.44$, where $r$ is the equivalent spherical diameter) and its isotropic shape, the absorption correction was not applied for the database from HY2. A check for systematic absence of the collected diffraction intensity datasets under RP and 3.01 GPa indicated that the space groups before and after the phase transition were $Imm\bar{2}$ and $Pmn\bar{2}$, respectively. Since neither phase had a center of symmetry, Bijvoet pairs were not averaged for the structure refinements. Inconsistent equivalent reflections were removed according to the method of Blessing (1987), and weighted averages of the remaining equivalents were used as diffraction data. Outliers of $|F_0| - |F_o|$ were evaluated using the method of Angel et al. (2000). The structure parameters [atomic coordinates and isotropic/anisotropic atomic displacement parameters (ADPs)] of all atoms except those for hydrogen were refined. All the least-square calculations were performed using SHELXL-97 (Sheldrick and Schneider, 1997) and WIN_GX software (Farrugia, 1999). The initial structural parameters of hemimorphite at ambient conditions were taken from Seryotkin and Bakakin (2011). Neutral atomic scattering factors derived from the International Tables for Crystallography vol. C (2004) and the extinction effect was applied to all refinements. Anisotropic ADPs ($U_{anis}$) were applied for structural refinements of RP and 3.01 GPa, yielding $R_1 = 3.13$ and 7.12% respectively. In contrast, structure refinements of 3.72 GPa data were successful only when applying isotropic ADP ($U_{iso}$), which yielded $R_1 = 14.35\%$. The main information on structure refinements is listed in Table 1. All crystal structures were drawn by using VESTA ver. 3 (Momma and Izumi, 2011).

**RESULTS**

**Pressure response of lattice constants of hemimorphite**

Lattice constants of hemimorphite under high-pressure conditions are listed in Supplementary Table S1 (Supplementary Tables S1 and S2 are available online from https://doi.org/10.2465/jmps.210731), and pressure evolutions of each value are plotted in Figure 2. Bulk compression of the HY2 shows a smooth curve with increasing pressure (Fig. 2a). Regarding axial compression, the pressure derivatives of the $a$– and $c$-axial lengths exhibited no shift under this pressure range, while the absolute value of pressure derivative of the $b$-axial length increased within the pressure range (Figs. 2b–2d). These trends of bulk and axial compression are similar to those reported by Seryotkin and Bakakin (2011). A change in the pressure derivative of the $b$-axial length indicated a pressure–induced phase transition. In addition, Bragg reflection peaks breaking the systematic absence conditions of the body-centered lattice ($h + k + l = 2n + 1$ for $hkl$) were observed at 3.01 GPa (Fig. S1; Supplementary Figure S1 is available online from https://doi.org/10.2465/jmps.219731), confirming the pressure–induced phase transition. As described in the experimental procedures, the space groups of the before- and after-transition phases could be determined as $Imm\bar{2}$ and $Pmn\bar{2}$, respectively, due to systematic absences in the observed reflection intensity data.

**Satellite reflections**

After the phase transition, satellite peaks were observed near certain reflections. Oscillation photographs taken before and after the phase transition are shown in Figure 3a,
Table 1. Conditions of the data collections and the structural refinements

| Pressure [GPa] | RP  | 3.01 | 3.72 |
|---------------|-----|------|------|
| Data collection |     |      |      |
| Index limits | +h ± k ± l | ±h ± k ± l | ±h ± k ± l |
| 2θ_max [°] | 90  | 85   | 85   |
| Data input | | | |
| No. of measured refs. | 2134 | 2523 | 2474 |
| No. of refs. read in SHELXL-97 | 2043 | 790  | 837  |
| No. of unique refs. [Fo > 4σ(Fo)] | 2008 | 785  | 790  |
| Structural model | | |
| Space group | Imm2 | Pmn2 | Pmn2 |
| Temperature factor | anis. | anis. | iso. |
| No. of parameters | 45  | 74   | 33   |

R-factors

- $R_{max}$ [%] *
- $R_{sigma}$ [%]
- $R1$ [%]
- $w_{R}$
- $w_{R2}$ [%]
- Goof
- Flack parameter

* Calculated before merging equivalents.

$R_{max} = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$

$R_{sigma} = \frac{\sum \sigma(F_o)}{\sum F_o}$

$R1 = \frac{\sum (F_o^2 - F_c^2)^2}{\sum F_o^2}$

Goof = $\sum (F_o^2 - F_c^2)^2$ / $n-p$)

Figure 2. Variation of the lattice constants of hemimorphite under compression. Closed symbol, this study; open symbol, Seryotkin and Bakakin (2011). 1σ of the parameter is smaller than the radius of the circle.
which is magnified around a peak with satellite reflections. Peak profiles of 520 reflection scanned along the $b'$ direction (41 steps with a step width of $\Delta k = 0.01$) at several pressure points are shown in Figure 3b. Pairs of satellite reflections were observed at the $\Delta k \approx \pm 0.12$ position away from the respective Bragg peaks, and no other satellite reflections with a different modulation vector $q$ were detected. The magnitude of $q$ showed $|q| = |\Delta k \cdot b'| \approx 1/(8.4b) \approx 1/90 \, \text{Å}^{-1}$, which did not change under conditions 3.01-4.70 GPa (Fig. 3b). Importantly, Bragg reflections with satellite peaks broke the systematic absence rules of $I$-lattice and satisfied those of $Pmn2$: i.e., $h+k+l = 2n+1$ for $hkl$; $k+l = 2n$ for $0kl$; and $h+l = 2n$ for $h0l$.

Structure information

Compared with a non-modulated structure model (Ser- yokhin and Bakakin, 2011), the structure that was refined only with the intensity data of the Bragg reflections exhibited split atomic positions or more elongated displacement ellipsoids due to overlap among lattices with slight structural difference, and thus should be treated as an average structure. The final atomic coordinates and isotropic/equivalent ADPs ($U_{\text{iso}}/U_{\text{eq}}$) under RP, 3.01 and 3.72 GPa are summarized in Table 2, and ADP $U_{\text{min}}$ for RP and 3.01 GPa conditions are summarized in Table S2. Although a minor amount of phosphorus detected by chemical analyses was applied to refine the site occupancy parameter at the Si sites, there was no improvement on convergence with the $Imm2$-structure. Therefore, phosphorus was ignored in all structural analyses. The occupancy at the O5 site that forms the water molecule did not decrease in the $Pnn2$-structure, which indicated that no dehydration occurred by compression. The lengths of the principal axes ($W_{11} \geq W_{22} \geq W_{33}$) on the anisotropic ADPs and the unit vectors of those for each site under RP and 3.01 GPa are summarized in Table 3, and the displacement ellipsoids at all sites at both pressure points are depicted in Figure 4. Next, we refer to the differences between the parameters of the $Imm2$-structure under RP and the $Pnn2$-structure at 3.01 GPa. When the difference in $U_{\text{eq}}$ between the $Imm2$- and $Pnn2$-structures ($\Delta U_{\text{eq}}$) exceeded 3σ, the configuration of the displacement ellipsoid was described below with the aspect ratio of the principal axes ($r_{\text{anis}} = W_{11}/W_{33}$) and the direction of the major axis $W_{11}$ (see Tables 2 and 3).

The $U_{\text{eq}}$ values at the Zn1 and the Zn2 displacement ellipsoids in the $Pnn2$-structure were remarkably larger than that of the Zn displacement ellipsoids in the $Imm2$-structure [$\Delta U_{\text{eq}} = 0.0111(12) \, \text{Å}^2$ for Zn1 and $\Delta U_{\text{eq}} = 0.0120(12) \, \text{Å}^2$ for Zn2]. Although the direction of elongation for the ellipsoids lies between the $a$- and $b$- axes both in the structures, they exhibited greater elongation at the $Pnn2$-structure [$r_{\text{anis}} = 1.61(7)$ for Zn1 and $r_{\text{anis}} = 1.54(6)$ for Zn2] than that at the $Imm2$-structure [$r_{\text{anis}} = 1.242(5)$]. The $\Delta U_{\text{eq}}$ at the Si site was 0.011(3) $\, \text{Å}^2$. The displacement ellipsoid at the Si site was almost spherical in the $Imm2$-structure [$r_{\text{anis}} = 1.08(3)$]. However, in the $Pnn2$-structure, the ellipsoid was elongated along the $b$-axis [$r_{\text{anis}} = 1.75(16)$]. The O1 site in the $Imm2$ structure was distinguished as the O11 and O12 sites in the $Pnn2$-structure. The $\Delta U_{\text{eq}}$ at the O12 site was 0.027(8) $\, \text{Å}^2$, which was more significant than that at the O11 site [0.015(8) $\, \text{Å}^2$]. Likewise, the displacement ellipsoid at the O12 site was elongated compared to that at the O11 site [$r_{\text{anis}} = 1.73(4)$ for O1, $r_{\text{anis}} = 3.01(19)$ for O11 and
Unlike the sites described above, the displacement ellipsoids at the O3 and the O5 sites did not show unambiguous value in the $\Delta U_{eq}$.

Cation–oxygen distances, cation–oxygen–cation angles, and O…O distances that were potentially associated with the hydrogen bonds under RP and 3.01 GPa are listed in Table 4, together with the referenced values from Sergeykin and Bakakin (2011) under RP (the $Imm_2$–structure) and 3.17 GPa (the $Pnn_2$–structure). First, to assess the deformation of the coordination tetrahedra that occurred through the phase transition, the distortion index $D = \frac{\sum_i |l_i - l_{av}|}{4l_{av}}$ in Baur (1974) was calculated for each bond distance $l_i$ ($i = 1-4$) as well as the averaged bond distance $l_{av}$ of the coordination tetrahedra. The $D$ value of the SiO$_4$ tetrahedra was 0.0027(6) in the $Imm_2$–structure and 0.007(4) in the $Pnn_2$–structure. Meanwhile, in the $Imm_2$–structure, the distortion index of the ZnO$_4$ tetrahedron was 0.0064(4), where the Zn sites diverge into Zn1 and Zn2 after the phase transition; in the $Pnn_2$–structure, the $D$ value of the Zn1–tetrahedron was 0.010(5) and that of the Zn2–tetrahedron was 0.008(5). Unambiguous gaps of the $D$ values for the Zn– and the Si–tetrahedron between the two structures were not confirmed within the error.

The angle evolution from RP to 3.01 GPa is described below as $\Delta$Si–O–Si, $\Delta$Si–O–Zn and $\Delta$Zn–O–Zn. The increases in the two joint angles between the ZnO$_4$ tetrahedron building up the same four-membered ring, $\Delta$Zn(1)–O2–Zn(2) and $\Delta$Zn(1)–O3–Zn(2), were +0.5(5)$^\circ$ and −2.6(10)$^\circ$, respectively. The angle change in the Si2O$_7$ dimer $\Delta$Si–O4–Si was −5.0(14)$^\circ$. Summing up the three kinds of angle variations mentioned above, SBU would be nearly flattened along the line joining the two Si sites (parallel to the $b$–axis of the $Imm_2$ structure).

Within the framework of hemimorphite structure, a Zn–polyhedron shares the corner (O1 or O2 site) with a Si–polyhedron. The Zn–O1–Si angle within SBU diverge into two types of the bond angles after the phase transition in response to the splitting of the Zn and O1 sites. The angle variations $\Delta$Zn(1)–O1(1)–Si and $\Delta$Zn(2)–

### Table 2. Atomic positions and equivalent/isotropic displacement parameters of hemimorphite under each pressure

| Site | Wyckoff position | $x/a$  | $y/b$  | $z/c$  | $U_{eq}$  |
|------|------------------|--------|--------|--------|----------|
| Zn   | 8e               | 0.20457(2) | 0.16117(2) | 0      | 0.01039(5) |
| Si   | 4d               | 0      | 0.14627(5) | 0.5067(2) | 0.00732(8) |
| O1   | 8e               | 0.16021(17) | 0.20545(13) | 0.6360(3) | 0.01290(19) |
| O2   | 4d               | 0      | 0.16655(19) | 0.1940(4) | 0.0121(3)  |
| O3   | 4c               | 0.3052(3) | 0      | 0.0405(6) | 0.0210(6)  |
| O4   | 2a               | 0      | 0      | 0.5913(6) | 0.0141(4)  |
| O5   | 2b               | 1/2    | 0      | 0.5188(18) | 0.076(3)  |

3.01 GPa

| Zn1  | 4c               | 0.22227(14) | 0.1525(3) | 0      | 0.0226(13) |
| Zn2  | 4c               | 0.30458(15) | 0.3368(3) | 0.4971(6) | 0.0232(13) |
| Si   | 4c               | 0.0122(3)   | 0.1448(7) | 0.5105(12) | 0.020(3)   |
| O11  | 4c               | 0.1797(13)  | 0.195(2)  | 0.632(2)  | 0.037(9)   |
| O12  | 4c               | 0.3551(13)  | 0.288(3)  | 0.1371(19) | 0.047(10)  |
| O2   | 4c               | 0.0125(11)  | 0.160(2)  | 0.1923(17) | 0.033(10)  |
| O3   | 4c               | 0.3152(9)   | 0.9899(18) | 0.040(2)  | 0.019(9)   |
| O4   | 2a               | 0      | 0      | 0.610(3) | 0.030(15) |
| O5   | 2b               | 1/2    | 0      | 0.525(4) | 0.069(18) |

3.72 GPa

| Zn1  | 4c               | 0.24547(2) | 0.1418(5) | 0      | 0.0200(6) |
| Zn2  | 4c               | 0.32688(2) | 0.3292(5) | 0.4935(8) | 0.0198(6) |
| Si   | 4c               | 0.0317(5)  | 0.1432(10) | 0.5072(18) | 0.0173(9) |
| O11  | 4c               | 0.2109(15) | 0.174(3)  | 0.636(3)  | 0.018(2)   |
| O12  | 4c               | 0.3897(16) | 0.271(4)  | 0.134(3)  | 0.023(3)   |
| O2   | 4c               | 0.0322(16) | 0.156(3)  | 0.186(3)  | 0.022(3)   |
| O3   | 4c               | 0.3155(14) | 0.988(4)  | 0.045(3)  | 0.021(3)   |
| O4   | 2a               | 0      | 0      | 0.605(4) | 0.018(3)   |
| O5   | 2b               | 1/2    | 0      | 0.511(8) | 0.039(5)   |

$r_{anis} = 2.3(3)$ for O12]. Unlike the sites described above, the displacement ellipsoids at the O3 and the O5 sites did not show unambiguous value in the $\Delta U_{eq}$.
O1(2)–Si were −0.3(8)° and −1.5(8)°, respectively (Figs. 4c and 4d). In comparison with the values from Seryotkin and Bakakin (2011) \[ \Delta \text{Zn}(1)–\text{O}1(1)–\text{Si} = −1.3(3)° \] and \[ \Delta \text{Zn}(2)–\text{O}1(2)–\text{Si} = −3.4(3)° \], the absolute amount of \[ \Delta \text{Zn}(2)–\text{O}1(2)–\text{Si} \] were apparently smaller than that if the pressure difference (3.01 and 3.17 GPa) was considered. The variations \[ \Delta \text{Zn}(1)–\text{O}2–\text{Si} \] and \[ \Delta \text{Zn}(2)–\text{O}2–\text{Si} \] were −0.3(6)° and +0.5(6)°, respectively. The changes in the four joint angles (\[ \Delta \text{Zn}1–\text{O}12–\text{Si} \], \[ \Delta \text{Zn}2–\text{O}11–\text{Si} \], \[ \Delta \text{Zn}1–\text{O}11–\text{Zn}2 \] and \[ \Delta \text{Zn}1–\text{O}12–\text{Zn}2 \]) that formed from the neighboring SBU between the \( \text{Imm}2 \) and the \( \text{Pnn}2 \) structures were +1.4(13)°, −3.2(12)°, +1.1(9)°, and +0.7(9)°, respectively (Figs. 4c and 4d). Among them, the joint angle variation [+1.4(13)°] between the Zn1– and Si-polyhedra \( \text{AZn}1–\text{O}12–\text{Si} \) from our results was significantly lower than that [+4.5(4)°] from Seryotkin and Bakakin (2011).

### DISCUSSION

**Cause of satellite peak appearance**

Since satellite reflections were invariably observed above 3.01 GPa at a position that \( k \approx n \pm 1/8.4 \) (Fig. 3b), the \( \text{Pmn}2 \) phase contained long-period factors that resulted in a modulation along the [010] direction. Until 2.46 GPa, our hemimorphite samples used for in situ high-pressure experiments showed no satellite reflections associated with a modulated structure (Fig. S1). This means that the satellites were caused by the phase transition process. Based on the results from structural refinements, all the site occupancies showed no decrease due to compression or impurity. This fact implies that satellite peaks had been originated from a structural modulation such as periodic displacement of atomic positions rather than a compositional modulation such as the distribution of minor ele-

| Site | Rmsd* [Å] | Unit vector | 3.01 GPa (Pmn2-structure) | Rmsd* [Å] | Unit vector |
|------|------------|-------------|--------------------------|------------|-------------|
| Zn(1) | \( w_{11} \) | 0.1144(3) | [−0.65, 0.75, 0.03] | 0.190(7) | [−0.63, 0.78, 0.02] |
|      | \( w_{22} \) | 0.0979(4) | [ 0.11, 0.05, 0.99] | 0.133(7) | [ 0.62, 0.48, 0.62] |
|      | \( w_{33} \) | 0.0922(4) | [ 0.75, 0.65,−0.11] | 0.118(7) | [−0.48,−0.40, 0.78] |
| Zn(2) | \( w_{11} \) | 0.1492(17) | [−0.61, 0.77, 0.22] | 0.28(4) | [−0.53, 0.85,−0.04] |
|      | \( w_{22} \) | 0.095(2) | [−0.05,−0.31, 0.95] | 0.14(3) | [ 0.76, 0.45,−0.48] |
|      | \( w_{33} \) | 0.086(3) | [ 0.79, 0.56, 0.23] | 0.12(2) | [ 0.38, 0.29, 0.88] |
| Si   | \( w_{11} \) | 0.0889(17) | [ 0.00, 0.59, 0.81] | 0.17(3) | [ 0.07, 0.98, 0.16] |
|      | \( w_{22} \) | 0.0852(9) | [ 1.00, 0.00, 0.00] | 0.138(4) | [ 0.99,−0.09, 0.12] |
|      | \( w_{33} \) | 0.0825(18) | [ 0.00, 0.81,−0.59] | 0.100(7) | [−0.13,−0.15, 0.98] |
| O1(1) | \( w_{11} \) | 0.1492(17) | [−0.61, 0.77, 0.22] | 0.28(4) | [−0.53, 0.85,−0.04] |
|      | \( w_{22} \) | 0.095(2) | [−0.05,−0.31, 0.95] | 0.14(3) | [ 0.76, 0.45,−0.48] |
|      | \( w_{33} \) | 0.086(3) | [ 0.79, 0.56,−0.23] | 0.12(2) | [ 0.38, 0.29, 0.88] |
| O1(2) | \( w_{11} \) | 0.142(3) | [ 0.00, 0.99, 0.17] | 0.25(6) | [−0.03, 1.00, 0.03] |
|      | \( w_{22} \) | 0.096(3) | [ 1.00, 0.00, 0.00] | 0.150(12)| [ 0.99,−0.04,−0.09] |
|      | \( w_{33} \) | 0.083(5) | [ 0.00,−0.17, 0.99] | 0.108(12)| [ 0.10,−0.03, 1.00] |
| O2   | \( w_{11} \) | 0.189(4) | [−0.37, 0.00, 0.93] | 0.177(19)| [−0.26, 0.36, 0.90] |
|      | \( w_{22} \) | 0.123(4) | [ 0.93, 0.00, 0.37] | 0.14(3) | [ 0.89, 0.44, 0.09] |
|      | \( w_{33} \) | 0.110(3) | [ 0.00, 1.00, 0.00] | 0.08(12)| [−0.36, 0.82,−0.43] |
| O3   | \( w_{11} \) | 0.141(4) | [ 1.00, 0.00, 0.00] | 0.21(8) | [−0.59, 0.81, 0.00] |
|      | \( w_{22} \) | 0.127(4) | [ 0.00, 1.00, 0.00] | 0.15(6) | [ 0.81, 0.59, 0.00] |
|      | \( w_{33} \) | 0.077(5) | [ 0.00, 1.00, 0.00] | 0.14(18)| [ 0.00, 0.00, 1.00] |
| O4   | \( w_{11} \) | 0.39(12) | [ 0.00, 1.00, 0.00] | 0.39(7) | [ 0.24, 0.97, 0.00] |
|      | \( w_{22} \) | 0.225(8) | [ 1.00, 0.00, 0.00] | 0.18(2) | [ 0.97,−0.24, 0.00] |
|      | \( w_{33} \) | 0.159(10) | [ 0.00, 0.00, 1.00] | 0.14(3) | [ 0.00, 0.00, 1.00] |

* Rmsd, root mean square displacement (= the lengths of the principal axes of a displacement ellipsoid of 68.3% probability).
ments or vacancies. Seryotkin and Bakakin (2011) reported that the structural developments through the phase transition include the rotation of the SBU, corresponding deformation of the channels, and re-configuration of hydrogen positions in the channels. In this study, fluctuation in the atomic position can be caused by the developed structural components as noted above. Furthermore, since Bragg reflections accompanied by satellite reflections break the systematic absence rule of $I$-lattice and satisfy the appearance of satellite peaks is associated with the O1 and Zn sites, which was divided into two sites after the phase transition. Although it is highly possible that behavior of hydrogen would be involved with modulation in the $Pmn2$ structure, such as the reported modulation of hemimorphite under a low-temperature condition (Libowitzky et al., 1998), the hydrogen positions are hardly observable with XRD, especially under high-pressure conditions. Therefore, in this discussion,
the effect of hydrogen on modulation is not considered. Further experiments such as a neutron diffraction experiment are required to elucidate these effects.

**Averaged structure of the high-pressure phase of hemimorphite**

In this study, there were little variations in the bond angles Zn(2)–O1(2)–Si and Zn(1)–O1(2)–Si between RP and 3.01 GPa. According to the non–modulated structure, these angles originally showed steep changes across the transition boundary as well as the rotation angle of SBU (Seryotkin and Bakakin, 2011). The difference in the bond angle variations indicates that the SBU rotation in the averaged structure was also undervalued. Therefore, by focusing on the rotation angle ($\Phi$) of SBU, the averaged structure model with modulation in this study was compared with the non–modulated structure. Here the rotation angle $\Phi$ was defined as the angle between the O3–O3' vector and the $a$-axis. $\Phi > 0^\circ$ when the SBU on the center rotates anticlockwise on $-c$ (Fig. 5a). Before the phase transition, the O3–O3' vector was parallel to the $a$-axis, and then $\Phi = 0^\circ$. With assumptions that (1) the increase of $\Phi$ was linear just after the phase transition during compression, and that (2) the phase boundary was 2.5 GPa, the estimated $\Phi$ at each pressure could be calculated from the results of Seryotkin and Bakakin (2011). The observed $\Phi$ of this sample was 2.39(7)$^\circ$, which was 57% of the estimated angle 4.169(18)$^\circ$. In addition, although compression of the $b$-axis was mostly enhanced by the rotation of SBU, presence or absence of the modulation yielded no difference in the axial compression. These considerations imply that modulation in the $Pnn2$ structure would cause the development of the averaged structure, in which SBU rotation was seemingly limited. An SBU has two states that are associated with each other due to the translation between the origin and the body center (Figs. 5a and 5b). After the phase transition, the SBU on the origin and that at the center–body positions rotated in normal and opposite directions, re-

| M–O distances [Å] | RP | This study | Seryotkin and Bakakin (2011) |
|-------------------|----|------------|-----------------------------|
| Si–O1(1)          | 1.6239(15) | 1.592(14) | 1.6238(19) |
| Si–O1(2)          | equiv. | 1.601(16) | equiv. | 1.604(5) |
| Si–O2             | 1.613(2)  | 1.614(1)  | 1.615(3)  | 1.618(5) |
| Si–O4             | 1.627(11) | 1.623(9)  | 1.627(12) | 1.617(3) |
| Zn(1)–O1(1)       | 1.9560(14) | 1.941(12) | 1.964(2)  | 1.965(4) |
| Zn(2)–O1(2)       | equiv. | 1.935(12) | equiv. | 1.953(4) |
| Zn(1)–O1(2)       | 1.9518(11) | 1.93(2)   | 1.955(18) | 1.922(5) |
| Zn(2)–O2           | equiv. | 1.942(2)  | equiv. | 1.936(5) |
| Zn(1)–O3           | 1.9338(11) | 1.900(18) | 1.9315(11) | 1.922(5) |
| Zn(2)–O3           | equiv. | 1.912(17) | equiv. | 1.912(5) |

| M–O–M angles [°] |
|------------------|
| Si–O4–Si         | 149.2(2)  | 144.1(13) | 149.3(2)  | 144.6(4) |
| Zn(1)–O3–Zn(2)   | 126.70(7) | 124.1(10) | 126.85(7) | 123.1(3) |
| Zn(1)–O2–Zn(2)   | 119.75(5) | 120.3(5)  | 119.61(7) | 121.0(3) |
| Si–O2–Zn(1)      | 119.51(9) | 119.2(5)  | 119.62(12) | 118.7(3) |
| Si–O2–Zn(2)      | equiv. | 120.6(6)  | equiv. | 119.9(3) |
| Si–O1(1)–Zn(1)   | 116.68(9) | 116.4(8)  | 116.91(12) | 115.6(3) |
| Si–O1(2)–Zn(2)   | equiv. | 115.2(8)  | equiv. | 113.5(3) |
| Zn(1)–O1(1)–Zn(2)| 114.00(7)| 115.3(9)  | 113.88(9) | 115.3(2) |
| Zn(2)–O1(2)–Zn(1)| equiv. | 114.7(9)  | equiv. | 113.7(2) |
| Si–O1(1)–Zn(2)   | 128.32(9) | 125.1(12) | 128.29(12) | 123.1(3) |
| Si–O1(2)–Zn(1)   | equiv. | 129.8(13) | equiv. | 132.8(4) |

| O–O distances [Å] |
|------------------|
| O3..O5           | 2.939(8)  | 2.88(2)   | 2.948(9)  | 2.837(14) |
| O3..O3'          | 3.260(3)  | 3.042(11) | 3.276(3)  | 3.023(8)  |
| O5..O3''         | 3.125(9)  | 3.005(13) | 3.141(9)  | 3.047(10) |
| O5..O1(1)        | 3.647(3)  | 3.382(19) | 3.658(2)  | 3.200(6)  |
| O5..O1(2)        | equiv. | 3.716(19) | equiv. | 3.920(6)  |

1) $A'$, ($-x+1, -y, z$). 2) $A''$, ($x, y, z+1$).
spectively. When looking down along the $c$-axis, the SBU on the center of the unit cell shown in Figure 5a rotated anticlockwise (normal direction), whereas the SBU shown in Figure 5b rotated clockwise (opposite direction). The alternating rotation of an SBU from normal to the opposite direction (or opposite to normal) is equal to the phase inversion, and the presence of anti-phase boundaries (APB) could be presumed. The APBs observed at some phase transitions were followed by a reduction of symmetry. For example, the α-β phase transition of quartz causes APBs upon cooling within a limited temperature range (Dolino et al., 1983). Here, the unit cells with a normal phase and opposite phase will be called ‘p’ and ‘n’, respectively. The coherency between the anti-phases could result in the averaged structure and insufficient rotation angle of the SBU $\Phi'$ (Fig. 5c).

**Model of the modulation**

The configuration of the APBs resulting in the $Pn\bar{n}2_1$-structure can be determined from the characteristics of the satellite peaks. According to Korekawa (1964), a diffraction pattern with first-order satellites is yielded when the scattering factor of each site is described as a uniform sinusoidal wave function along a single direction. To apply the consideration of the sinusoidal wave of the scattering factors to the $Pn\bar{n}2_1$-structure model with APBs, several problems must be solved. (1) If the regularity of the APBs spans the whole range of the sample, the fraction of p-cells is equal to that of n-cells. (2) The fluctuating parameters result from neither impurities nor deficiencies but displacements of the atomic sites. (3) Some Bragg reflections are not accompanied by satellites. (4) Assuming that the APBs of the $Pn\bar{n}2_1$-structure line up at a regular interval, higher-order satellites should also be spotted. To deal with problem (1), the sample at 3.01 GPa should be divided into two types of domains: a domain with and without the coherency across the APBs. In the incoherent domain, the direction of SBU rotation is indistinguishable on the XRD experiments, and the coherent domain should be observed as the averaged structure of p- and n-cells. Problem (2) can be resolved by introducing the periodic function $\eta(y)$, which represents the displacements of each site involved in SBU rotation along the $b$-axis. The value of $\eta(y)$ for p- and n-cells is +1 and −1, respectively. When $\eta(y) = 0$, all the atomic positions are fully ordered and the symmetry is $Imm2$. Within the coherent domain, the $\eta(y)$ is depicted as a sinusoidal function with the periodicity $1/|q| = 8.4b \approx 90$ Å (Fig. 6), whereas the $\eta(y)$ deserves as a constant function in the incoherent domain. The presence or absence of the satellites described in problem (3) is explained by which domain yields an element of the diffraction pattern. For the coherent domain, the Bragg peaks that are consistent with the reflection conditions of $Imm2$ are not accompanied by any satellites due to the coherency and phase lag ($=\pi$) between p- and n-cells. As for the Bragg reflections that are consistent with $Pn\bar{n}2_1$ $(k + l = 2n$ for $0kl$ or $h + l = 2n$ for $hk0$) but inconsistent with $Imm2$ $(h + k + l = 2n + 1$ for $hkl$), the satellites show constructive interference only in the coherent domain, whereas the main peak is solely observable in the incoherent domain. Regarding problem (4), if the APB’s intervals are distributed with a mean value 90 Å (solid line in Fig. 6), the displacement $\eta(y)$ is approximated as the first-harmonic (dotted line in Fig. 6).

The $\Delta U_{eq}$ at the several sites (Zn1, Zn2, Si, and O12) had significant values in this study, and the $r_{anis}$ values also increased until 3.01 GPa. However, the elongation of these ellipsoids in the $Pn\bar{n}2_1$-structure was not coincident with displacements in the function $\eta(y)$, and the $U_{eq}$ at the O3 site showed no increase under compres-

![Figure 5](image-url)
tion. Therefore, the higher $U_{eq}$ values and the greater elongation for some atomic sites could be caused by the deformation of SBU within the APB.

Modulated structures yielding pairs of satellite reflection were also reported in the intermediate phase of the high-temperature phase transitions of NaNO$_2$ and β-eucryptite (Böhm, 1983). In both cases, the modulation period $M (= 1/|q|)$ increased while the intensities of the satellites decreased under heating conditions (Hoshino and Motegi, 1967; Press et al., 1980). Referring to the similarity between the effects of cooling and compression on crystal structures, both the $|q|$ value and the intensities of the satellite peaks might increase under compression of hemimorphite. Despite this expectation, the $M$ value in this study did not visibly change up to 4.70 GPa. This invariability indicates that the mobilization of the APBs had frozen under a certain pressure point between 2.46 and 3.01 GPa. The distribution of p- and n-cells (i.e., the direction of SBU rotation) was initially considered to be inhomogeneous. However, anisotropic elimination process had caused APBs developed along the $b$-axis. The presence of APBs in each domain relies on whether the elimination of the APBs had been accomplished prior to further SBU rotation and caused the structural compaction to progress. Below 3.01 GPa, the elimination process had been aborted. The difference in the domains is considered to be influenced by external factors such as the compression rate.

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**SUPPLEMENTARY MATERIALS**

Color version of Figures 1 and 3–6, Supplementary Figure S1, and Tables S1 and S2 are available online from https://doi.org/10.2465/jmps.210731.

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