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Structural modulation of hemimorphites under high-pressure

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1 Introduction

Hemimorphite, $Zn_4Si_2O_7(OH)_2{\cdot}H_2O$, has a structure of a three-dimensional framework composed of Si- & Zn-tetrahedra. The framework of hemimorphite is interpreted as accumulated secondary building units (SBU), and each of SBU is composed of a four-membered ring of ZnO_4 and a Si_2O_7 dimer [1]. Hemimorphite undergoes a pressure-induced phase transition (from *Imm*2 to *Pnn*2) explained by anti-clockwise rotation of the SBU at the origin and clockwise rotation of the SBU at the body-center [1].

We conducted in-situ single-crystal X-ray diffraction experiments to elucidate compressive behavior of the framework including the SBU at the high-pressure phase.

2 Experiment

Hemimorphite samples were from Yunnan, China. The averaged chemical formula is $Zn_{4.007(12)}$ $[(Si_{1.977(7)}P_{0.016(4)})O_7](OH)_2 \cdot H_2O$. The sample HY1 (60×80×70 μm^3 in size) was used for the experiment under room condition, and the sample HY2 (80×70×60 μm^3 in size) was sealed into a Merrill-Bassett type diamond anvil cell with the culet face 600 μm in diameter. A 4:1 methanol-ethanol fluid mixture and stainless disk with a 200 μm hole was used as a pressure-medium and a gasket, respectively. Pressure was calculated from the ruby fluorescence shift [2].

Diffraction data were measured with a vertical-type four-circle diffractometer installed in the beam line BL-10A, Photon Factory, High Energy Accelerator Research Organization, KEK. The wavelength of the beam was calibrated by the unit-cell volume of a NIST ruby standard crystal (SRM1990) at room condition. The unit cell parameters were refined at each pressure point. Since satellite peaks were observed above the transition point, reciprocal scans along the modulation vector ***q*** were conducted. Intensity data of the main Bragg reflections were collected at room pressure, 3.01 and 3.72 GPa. Though intensities of the satellite reflections were collected at 3.72 GPa, they were not used for structure refinements. Width and step of the omega scans is 0.7˚ and 0.01˚, respectively. The counting time is 0.5 second per step. Structure refinements were carried out by using the SHELXL97 [3]. At room pressure and 3.01 GPa, anisotropic displacement parameters (ADPs) were successfully refined. The conditions of the intensity collection and the refinements are listed in Table 1.

3 Results and Discussion

Fitted line of ***b***-axis compression obviously bends at 2.6 GPa (Fig. 1). The shift of axial compression at the pressure-induced phase transition agrees with Seryotkin and Bakakin (2011) [1]. The modulation vector ***q*** of the satellite reflections is approximately ±***b****/8.5 at any pressure points above 2.6 GPa. The satellite peaks belong to the Bragg peaks breaking the reflection condition of *I*-lattice. The intensity ratios between the satellites and the main Bragg peaks shows the almost constant value (~0.41).

Table 1. Parameters of the data collection and the structural refinement.

Run no.	H119-00	H117-2	H117-4
Pressure [GPa]	0.001	3.01	3.72
Data collection			
Index limits	$+h+k\pm l$	$\pm h\pm k\pm l$	$\pm h\pm k\pm l$
$2\theta_{max}$	90°	85°	85°
No. of measured refs.	2134	2523	2474
No. of refs. read in SHELXL-97	2043	790	837
No. of unique refs. $[F_o > 4\sigma(F_o)]$	2008	785	790
Structural model			
Space group	*Imm*2	*Pnn*2	*Pnn*2
Temperature factor	anis.	anis.	iso.
No. of parameters	45	74	33
R-factors			
R_{int} [%]	-	4.46	4.98
R_{sigma} [%]	1.54	1.83	2.71
$R1$ [%]	3.13	7.12	14.35
w_a	0.0516	0.1030	0.1000
w_b	0.35	6.69	-
$wR2$ [%]	8.11	19.40	37.26
Goof	1.105	1.122	2.967
Flack *x*	0.025(17)	0.07(8)	0.05(9)

$R_{int} = \Sigma\,|F_o^2 - F_o^2(\text{mean})|\,/\,\Sigma\,[F_o^2]$
$R_{sigma} = \Sigma\,[\sigma(F_o^2)]\,/\,\Sigma\,[F_o^2]$
$R1 = \Sigma\,\big||F_o| - |F_c|\big|\,/\,\Sigma\,|F_o|$
$w = 1\,/\,[\sigma^2(F_o^2) + (w_aP)^2 + w_bP]$ where $P = [2F_c^2 + \text{Max}(F_o^2, 0)]\,/\,3$
$wR2 = \{\Sigma\,[w(F_o^2 - F_c^2)^2]\,/\,\Sigma\,[w(F_o^2)^2]\}^{1/2}$
$Goof = \{\Sigma\,[w(F_o^2 - F_c^2)^2]\,/\,(n-p)\}^{1/2}$

The SBUs at 3.01 GPa rotated by 2.39(7)˚ whereas the estimated value from Seryotkin and Bakakin (2011) [1] is 3.939(17)˚. The insufficient rotation of the SBU could be caused by domains with oppositely rotated SBUs.

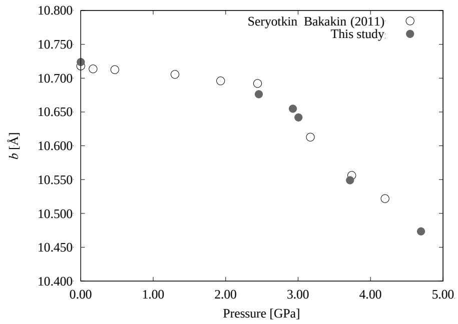

Fig. 1 Pressure dependence of *b* length.

References

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