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Pressure-induced phase transition of lawsonite into primitive lattice

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1 Introduction

A hydrous mineral lawsonite, $CaAl_2[Si_2O_7](OH)_2 \cdot H_2O$, is thought to be one of the water carrier into the upper mantle [1]. The space group of lawsonite under ambient condition is *Cmcm*.

Two pressure-induced phase transitions are known for lawsonite. The *C*-centered lattice of lawsonite turns into primitive orthorhombic (space group: unknown) above ~4 GPa [2], and subsequently into primitive monoclinic (space group: $P2_1/m$) around ~10 GPa [2,3].

Lawsonite at low-temperature occurs two reversible phase transitions at ~273 K and ~155 K. Previous single-crystal diffraction experiments using X-ray/neutron and the structural refinements revealed that the reduction of the symmetry is caused by optimization of H-bonds accompanied by rotation of H_2O and OH groups [5, 6].

For the single-crystal X-ray diffraction studies of both the phase transitions at 4 GPa and 273 K, 017 reflections were observed with the highest intensity among the reflections who were absent for the *C*-centered lattice [2, 6]. As long as the 4 GPa phase transition is second-order [2], the space group of the phase above 4 GPa is expected to be the subgroup of *Cmcm*. As the intensities of these reflections are weak, we conducted single-crystal X-ray diffraction experiments synthesized samples with synchrotron radiation.

2 Experiment

We synthesized the sample by using a 2,000-ton multi-anvil press in Geodynamics Research Center, Ehime University. The starting material was the mixture of $Ca(OH)_2$, $Al(OH)_3$ and SiO_2. The powder was compressed up to 10 GPa and was heated at 1,000 and 950 ˚C. Each temperature was kept for an hour. The run product contained several single-crystals of lawsonite.

X-ray diffraction experiments under high-pressure were obtained on a fragment measuring 50 × 50 × 40 μm^3. The sample was mounted on a Merrill-Bassett type diamond anvil cell with a 4:1 methanol-ethanol fluid mixture and a fragment of a natural ruby. A stainless-steel disk with a 200 μm hole was used as a gasket. Pressure was calculated from the ruby fluorescence line shift.

Diffraction data were measured with the automated four-circle diffractometer installed in the beam line BL-10A, Photon Factory, High Energy Accelerator Research Organization, KEK. The wavelength of the beam (λ = 0.70145 Å) was calibrated by the unit-cell volume of a NIST ruby standard crystal at room condition. Intensity data was collected on the orthorhombic HP phase up to 2θ = 70˚. Structural refinements were carried out by using the SHELXL97 [7] with WIN_GX software [8].

Moreover, ω-scans with 10 s/step were performed under various pressure especially on 017 and 3014 reflections who were useful for the reduction of the candidates for the space group and had relatively high intensities at the LT phase. To distinguish the reflections from those of the multiple diffraction of the diamonds, other scans were conducted with the offset angle of the goniometer head (φ angle) changed.

3 Results and Discussion

The 017 and 3014 reflections were observed above 1.5 GPa instead of 4 GPa. Changing the φ-offset angle by 15˚ did not weaken both of the reflections. Eventually, the intensity data were collected at 2.3 GPa. Table 1 shows the number of reflections which break the reflection conditions of *Cmcm*. Among the subgroups of *Cmcm* belonging to primitive orthorhombic, *Pmcn* and $P2_1cn$ satisfy the table. Thus, the space group of orthorhombic HP phase is restricted to these two.

The structural refinement with *Pmcn* provided the *R*1 value of 7.51 %, while the insufficient number of unique reflections disturbs the refinement with $P2_1cn$.

Table 1 Reflection conditions of *Cmcm*

		No. of observed reflections		
Symmetry operation	Reflection condition	breaking the condition	No. of scanning	Reflection condition is
C – lattice	$hkl : h + k = 2n$	41	448	broken
$2_1 \perp a$	$h00 : h = 2n$	0	0	-
$2_1 \perp b$	$0k0 : k = 2n$	0	13	preserved
$2_1 \perp c$	$00l : l = 2n$	0	19	preserved
n – glide$//c$	$hk0 : h + k = 2n$	0	25	preserved
n – glide$//b$	$h0l : h + l = 2n$	4	37	broken
b – glide$//a$	$0kl : k = 2n$	16	88	broken
c – glide$//b$	$h0l : l = 2n$	0	38	preserved

References

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