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Structural determination of the *Pmcn* lawsonite above 2 GPa

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1 Introduction

Lawsonite, $CaAl_2[Si_2O_7](OH)_2 \cdot H_2O$, can transport water from subduction zone into upper mantle on the benefit of its abundant water content (11.47 wt.%) and its efficient resistance to pressure [1].

Two high-pressure phases are known for lawsonite [2]. Whereas the monoclinic phase ($P2_1/m$) in the higher-pressure range (>10 GPa) is well-understood by diffraction studies [3], the primitive orthorhombic phase (*Pmcn* or $P2_1cn$) in the lower-pressure range remains to be elucidated [2,4]. A single-crystal X-ray diffraction study on synthesized lawsonite reported lower phase boundary (~2 GPa) [4] than the pressure of ~4 GPa obtained from the experiments on a natural specimen [2].

The primal aim of this experiment is to determine the space group of the *P*-orthorhombic phase by structural refinements. We also refined the structures of natural sample above 2 GPa to discuss the vast gap of the phase boundary between natural and synthesized lawsonites.

2 Experiment

Synthesized samples were obtained by using a 2,000-ton multi-anvil press in Geodynamics Research Center, Ehime University. The powdered mixture of $Ca(OH)_2$, $Al(OH)_3$ and SiO_2 was compressed up to 10 GPa and was kept heated at 1,000 °C (1 h) and 950 °C (1 h). The run product contained single-crystals of ~300 μm in diameter. Lawsonite from Reed Ranch, California was used as a natural specimen. The chemical formula of the natural sample is $Ca_{1.00}(Al_{1.95}Fe_{0.05})[Si_{2.00}O_7](OH)_2 \cdot H_2O$ [5].

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 determined from the ruby fluorescence line shift.

Diffraction data were measured with an automated four-circle diffractometer installed in the beam line BL-10A, Photon Factory, High Energy Accelerator Research Organization, KEK. The wavelength of synchrotron radiation (λ = 0.7012 Å) was calibrated by the unit-cell volume of a NIST ruby at room condition. Structural refinements except for H-sites were carried out by using the SHELXL97 [6]. Neutral atom scattering factors and isotropic atomic displacement parameters were applied for the structure model. The inconsistent equivalents and inconsistent reflections were omitted before the final refinement. The conditions of the data collections and the results of the refinements are listed in Table 1.

3 Results and Discussion

The structural refinement with *Pmcn* model provides much better accordance with the diffraction data. The final structure model shows that displacement along *c*-axis of O1 (bridging two SiO_4 tetrahedra) and O5 (constituting H_2O) are opposite. Since both oxygens do not coordinate with Al-sites, the driving force of this phase transition may be [001] shear motion between the AlO_6 chains, which is different from the shearing of AlO_6 chain in the [100] direction occurring at the orthorhombic-to-monoclinic phase transition [3]. Above 2 GPa, the natural sample also underwent the same phase transition.

Table 1 Experimental parameters of the refinements

Sample description			
Origin	natural	synthestic	
Pressure [GPa]	2.30(2)	2.50(4)	
Size[μm^3]	$50 \times 50 \times 50$	$50 \times 40 \times 40$	
Lattice parameters			
a[Å]	5.816(5)	5.8082(14)	
b[Å]	8.727(3)	8.728(3)	
c[Å]	13.052(8)	13.051(4)	
V[Å^3]	662.5(7)	661.7(3)	
Data collection			
Index limits	$\pm h, -k, -l$	$\pm h, \pm k, \pm l$	
$2\theta_{max}$	75°	70°	
No. of measured reflections	738	3718	
Structure refinement			
Space group	*Pmcn*	*Pmcn*	$P2_1cn$
R_{sigma} [%]	1.88	1.88	1.96
No. of unique reflections[$F_o > 4\sigma(F_o)$]	268	656	1085
No. of parameters	39	39	61
$R1$ [%]	6.58	5.37	9.47
w_a	0.1456	0.0697	0.1965
w_b	-	4.20	6.36
$wR2$ [%]	17.96	13.29	27.70
Goof	1.116	1.105	1.120

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