

## High-pressure phase transition of lawsonite at ~4 GPa

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## 1 Introduction

Lawsonite,  $\text{CaAl}_2[\text{Si}_2\text{O}_7](\text{OH})_2 \cdot \text{H}_2\text{O}$ , contains ~11.45 wt.%  $\text{H}_2\text{O}$ , and has space group *Cmcm*. The wide P-T stability fields of lawsonite indicate the potential for transporting water into a depth of more than 200 km [1].

Single-crystal X-ray diffraction experiments at high pressure have been carried out to find two pressure-induced phase transitions of lawsonite [2-4]. The C-centered lattice of lawsonite is reduced to primitive orthorhombic above ~4 GPa [2], and subsequently turns into primitive monoclinic (*P2<sub>1</sub>/m*) at ~10 GPa [3, 4].

In the meantime, single-crystal X-ray diffraction experiments on lawsonite at low temperature revealed two reversible phase transitions at ~273 K and ~155 K [5]. The driving force of the low-temperature phase transition is rotation of the  $\text{H}_2\text{O}$  molecules and the OH groups, and is associated with the lineation of hydrogen bonds [5, 6].

Configurations of the hydrogens at high pressure are still unknown. Besides, the space group of lawsonite between ~4 and ~10 GPa is not determined. The phase transition near 4 GPa is associated with the shift of the hydrogen sites which provides little changes to the X-ray diffraction data [2]. Therefore, we challenged single-crystal X-ray diffraction experiments with synchrotron source to confirm the phase transition around 4 GPa.

## 2 Experiment

For the present investigation, well-shaped crystals of lawsonite from Novato, California were used. The average of 23 probe analyses (EDS) yielded the chemical formula,  $\text{Ca}_{0.99}(\text{Al}_{1.92}\text{Fe}_{0.05}\text{Ti}_{0.01})[\text{Si}_{2.03}\text{O}_7](\text{OH})_2\text{H}_2\text{O}$ , which is close to the ideal formula of lawsonite.

X-ray diffraction experiments at ambient and high-pressure condition were obtained on fragments measuring  $160 \times 160 \times 140 \mu\text{m}^3$  and  $100 \times 60 \times 30 \mu\text{m}^3$ , respectively. Diffraction data were collected with the automated four-circle diffractometer installed in the beam line BL-10A (PF). The wavelength of the beam ( $\lambda = 0.71250 \text{ \AA}$ ) was calibrated by the unit-cell volume of a NIST ruby standard crystal at room condition.

At the high-pressure experiments, the sample was mounted into a Merrill-Bassett type diamond anvil cell with a 4:1 methanol-ethanol fluid mixture, and using a stainless-steel gasket which has a  $200 \mu\text{m}$  hole. Pressure was calculated from the 3rd-order Birch-Murnaghan Equation of State of lawsonite [2].

Intensities of the certain  $h + k = \text{odd}$  reflections (017 / 015 / 234) were measured above 4 GPa to monitor the change of the lattice type and to discuss the relation between HP transition and LT transition. All structural

refinements were carried out by using the SHELXL97 [7] with WIN\_GX software [8].

## 3 Results and Discussion

The unit-cell parameters were determined at pressures up to 4.7(2) GPa (Table 1). The compressibility of each axis is substantially comparable with the value on the previous study referred to estimate the pressures [2].

At 4.0(1) and 4.7(2) GPa, weak 017 and 015 reflections were observed. Additionally, other  $h + k = \text{odd}$  reflections were detected in the dataset collected at 4.7(2) GPa. They indicate the phase transition from C-lattice to P-lattice, unless these reflections are multiple diffractions. As 017 and 015 reflections were observed 4.0(1) GPa, diffraction data between 3 and 4 GPa are required to determine the actual phase transition point.

As the local symmetries of the non-hydrogen atoms were kept until the other phase transition near 10 GPa [4], the Wyckoff position of H would control the variation of space group through the HP phase transition. Therefore, determination of the space group just above 4 GPa demands the configurations of the hydrogens. However, as long as the phase transition near 4 GPa is also characterized by the spontaneous strain of the lattice [2], structural refinements excluding H would provide us some information like discontinuous atomic shifts around 4 GPa. Especially, the shifts of oxygens with pressure would throw light on the prediction of the H positions.

Table 1. Lattice constants of lawsonite at various pressures

Pressure [GPa]	RP	1.0(1)	4.0(1)	4.7(2)
<i>a</i> [Å]	5.8534(12)	5.8370(11)	5.7949(14)	5.788(2)
<i>b</i> [Å]	8.797(3)	8.767(3)	8.699(2)	8.684(3)
<i>c</i> [Å]	13.126(4)	13.097(9)	13.006(9)	12.989(11)
<i>V</i> [Å <sup>3</sup> ]	675.9(3)	670.1(5)	655.6(5)	652.8(6)

## References

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