Crystallography

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Structural refinements on super hydrous phase B, $Mg_{10}Si_3H_4O_{18}$, under high-P conditions up to 7.2 GPa using single-crystal diffraction data

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Introduction

Super hydrous phase B (sup B), $Mg_{10}{}^{VI}Si^{IV}Si_2H_4O_{18}$, is known as one of the dense hydrous magnesium silicate minerals (DHMS). This phase is stable under high-PT conditions such as 30 GPa and 1500°C[1],[2]. DHMS phases have been paid attention to by their potentials for carrying H into the Earth's interior in cold slabs.

Sup B has hydrogen bonds in its structure[3]. Hydrogen bond should be significantly influenced on its thermodynamic properties under high-PT conditions. However, no detail of the positional information on H was obtained under high-PT conditions. We try to refine the hydrogen positions in sup B under high-P conditions using single crystal X-ray diffraction intensity data sets with changing conditions of collection.

High-pressure single-crystal X-ray diffraction measurements of sup B were conducted up to 7.2 GPa. In this paper, we reported the results of structural refinements and ME analysis of sup B up to 7.2 GPa including previous 0.7 GPa results.

Experimental Procedure

The sample used for this study was synthesized at 20 GPa and 1000°C kept for 4 hours using a Kawai type multi anvil apparatus installed in Gakushu-in University. A colorless single crystal of OH end member sup B (0.08 × 0.08 × 0.04 mm^3 in size) was mounted on a modified Merrill-Bassett type diamond anvil cell (DAC) with a small piece of a ruby crystal, which used for the pressure calibration. The 4:1 fluid mixture of methanol and ethanol was used for the pressure medium and a SUS301 stainless plate used for a gasket. Pressure was determined by the ruby fluorescence method. The wavelength of synchrotron radiation was calibrated by the unit cell volume of a ruby standard crystal (NIST, SRM1990) at 25°C.

The X-ray diffraction intensities were measured using an automated four-circle X-ray diffractometer installed at the beam line BL-10A, Photon Factory, High Energy Accelerator Research Organization. Table 1 shows the mode of data collection, lattice constants and refinement information. Corrections for background and Lorentz-polarization were applied to all measured reflections. After these corrections, the absorption correction of diamond anvil cell was applied to all intensity data. The symmetrically equivalent reflections were averaged by the Laue symmetry of *mmm*. Reflections having Fo>4.0σ(Fo) were used for the structure refinements. In this report, space group of sup B structure was *Pnnm*. Final agreement factors were shown in Table 1. All calculations were performed using SHELXL97[4]. PRIMA[5] was used for ME analyses. The initial phase for ME analysis was calculated from the results of structure analyses. In ME analyses, unit cell was divided into 48 × 140 × 88 sections. Reflections having Fo<1.5σ(Fo) did not use for ME analysis.

Results

The position and isothermal temperature factor of hydrogen could be refined at 0.7 and 5.7 GPa conditions, but could not refine at 3.5 and 7.2 GPa because of the scarce of observed reflections. The results at 0.7 GPa already reported[6]. Hydrogen located at x/a=0.939(7), y/b=0.308(5), z/c=0.104(4), U_{eq}=0.05(1) at 5.7 GPa. The O-H distance was 0.93(7)Å, which was consistent to that of sup B at ambient conditions (0.91(3)Å in our result and 0.89(2)Å[3]).

The results of ME analysis showed that the electron distribution of each atom in sup B structure was distributed widely along the *b*-direction because of 1) the geometrical effects of DAC and 2) the decrease of the number of observed reflection intensity data.

Table 1. Information on the mode of collection, lattice parameter and structural refinement

Pressure /GPa	0.0	0.7	3.5	5.7	7.2
Source	Shield-tube	Synchrotron	Synchrotron	Synchrotron	Synchrotron
wavelength /	0.7107 (MoKα)	0.6493	0.7014	0.6455	0.6455
Cell parameters	*a*= 5.099(1)	*a*= 5.095(1)	*a*= 5.063(1)	*a*= 5.033(1)	*a*= 5.023(1)
	b= 13.997(3)	*b*= 13.974(3)	*b*= 13.889(3)	*b*= 13.814(3)	*b*= 13.788(3)
	c= 8.722(2)	*c*= 8.707(2)	*c*= 8.655(2)	*c*= 8.612(2)	*c*= 8.596(2)
	V= 622.5 ^{3}	*V*= 619.9 ^{3}	*V*= 608.7 ^{3}	*V*= 598.8 ^{3}	*V*= 595.3 ^{3}
Space Group	*Pnnm*	*Pnnm*	*Pnnm*	*Pnnm*	*Pnnm*
maximum 2θ	60	70	70	75	75
sinθ/λ	0.704	0.883	0.818	0.943	0.943
measured refs.	939	552	474	689	558
refs. for refinement	86	86	38	86	65
parameters	2.2	2.8	3.2	3.4	3.3
R	6.1	6.8	6.9	7.5	8.1
wR^2	1.102	1.128	1.067	1.085	1.073
GoF	2.2	3.6	4.6	3.9	5.2
R_{int}					

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References

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