

LETTER

Crystal structure of parasibirskite (CaHBO_3) and polymorphism in sibirskite and parasibirskite

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The crystal structure of parasibirskite (CaHBO_3) obtained at Fuka, Okayama Prefecture, Japan, was determined by Monte Carlo simulation using powder X-ray diffraction data and confirmed by Rietveld refinement. Parasibirskite is monoclinic with space group $P2_1/m$ and cell constants $a = 6.722(4)$, $b = 5.437(2)$, $c = 3.555(2)$ Å, and $\beta = 93.00(5)^\circ$. The calcium atom is surrounded by seven oxygen atoms with a monocapped distorted trigonal prism arrangement. The edge-shared CaO_7 polyhedra form a layer structure elongated along the crystallographic b - and c -axes. These CaO_7 layers are connected to each other by BO_3 triangles, thus forming the parasibirskite structure. The hydrogen atom was presumed to connect to the O1 atom from the bond-valence calculation. Parasibirskite is a dimorph of sibirskite (CaHBO_3), which consists of CaO_6 double chains connected by BO_3 triangles.

Keywords: Parasibirskite, Sibirskite, CaHBO_3 , Crystal structure, Monte Carlo simulation

INTRODUCTION

A series of calcium borate and calcium borate hydroxide minerals such as takedaite, sibirskite, parasibirskite, uralborite, nifontovite, olshanskyite, frolovite, and pentahydroborite were discovered at Fuka, Okayama Prefecture, Japan (Kusachi and Henmi, 1994; Kusachi et al., 1994, 1995, 1997, 1998, 1999, 2000). These are hydrothermal alteration products of takedaite, and the concentration of H_2O varies with the formation temperature, as discovered by Hart and Brown (1962) from the hydrothermal synthesis of calcium borate compounds. Parasibirskite, CaHBO_3 , a new mineral, is a dimorph of sibirskite that was first reported in Fuka by Kusachi et al. (1998). The crystal structure of sibirskite was determined using Monte Carlo calculations by Miura and Kusachi (2008). However, the crystal structure of parasibirskite has not yet been clarified and the crystallographic relationship between these dimorph minerals is not known. In the present study, a Monte-Carlo-based simulation developed by Miura and Kikuchi (1999) is employed to solve an initial model for the crystal structure of parasibirskite using a set of d -values and intensity data reported by Kusachi et al. (1998).

Further, the crystal structure was refined by the Rietveld method, and these structures were compared from the viewpoint of the crystalline chemistry.

STRUCTURAL ANALYSIS

The crystal data for parasibirskite reported by Kusachi et al. (1998) are as follows: chemical formula, CaHBO_3 ($Z = 2$); cell constants, $a = 6.722(4)$, $b = 5.437(2)$, $c = 3.555(2)$ Å, and $\beta = 93.00(5)^\circ$; and space group, $P2_1/m$. The powder XRD data used for the structure refinement was collected using a Mac Science MX-Labo diffractometer with $\text{CuK}\alpha$ radiation (40 kV, 30 mA, 0.5° – 0.5° – 0.15 mm slit) in a step scanning mode over a 2θ range of 10 – 100° in increments of 0.02° (20 s/step). The X-ray intensity was counted after monochromatization by pyrolytic graphite. The measured XRD pattern includes the diffraction peaks of parasibirskite and sibirskite. The coordinates of the calcium and oxygen atoms were determined by the Structure Model-Assembly Program for an automated search of the optimal structure models to satisfy the observed XRD data, cell constants, space group, chemical formula, Z number, and interatomic distances. The two calcium atoms in a unit cell must be located in one of the following Wyckoff positions of $P2_1/m$ — $2a$, $2b$, $2c$, $2d$, or $2e$; the six

oxygen atoms must be located in three of the following Wyckoff positions— $2a$ – $2e$ —or one of the $2a$ – $2e$ positions and $4f$ general equivalent position. The search program automatically tested all possible combinations of two calcium and six oxygen atoms in the unit cell. The boron position was not determined by the search program because of its relatively low scattering factor. However, it was expected that the boron atoms would be located at the center of the oxygen triangles in the parasibirskite structure to form the BO₃ triangles, which is common in borate minerals such as takedaite (Ca₃[BO₃]₂; Schuckmann, 1969; Vegas et al., 1975) and sibirskite (CaHBO₃; Miura and Kusachi, 2008). The search procedures established by Miura et al. (2000) have been used for the present structural analysis. The temperature factors were fixed to reduce the calculation time. The obtained model exhibits an edge-shared CaO₇ sheet extending along the *b*- and *c*-axes.

STRUCTURAL REFINEMENT

The RIETAN-2000 program (Izumi and Ikeda, 2000) was used for the Rietveld refinement. The structure model obtained by employing the abovementioned Monte Carlo search was used as the initial parasibirskite structure. Linear constraints on the interatomic distances were not required in the calculation and the atomic coordinates and temperature factors of Ca, B, O1, and O2 atoms were refined. The hydrogen site could not be determined by the X-ray diffraction analysis. The background parameters, peak shift parameters, profile parameters, and cell constants were also optimized in the calculation. It should be noted that the crystal structure of sibirskite was also included in the present structural analysis. The atomic position and temperature factor for B atoms in sibirskite was fixed to the reported data (Miura and Kusachi, 2008). The final *R* values for pattern fitting are $R_{wp} = 10.91$ and $R_p = 8.18\%$, $S = 1.8461$. The *R* values based on the intensity and structure factors are $R_I = 4.03\%$ and 3.99% and $R_F = 2.36\%$ and 2.13% for parasibirskite and sibirskite, respectively. The results of the Rietveld refinement are shown in Figure 1. The obtained cell constants and structure data for sibirskite were reasonably consistent with the previous data (Miura and Kusachi, 2008). The cell constants of parasibirskite obtained by the Rietveld calculation, $a = 6.717(6)$, $b = 5.434(5)$, $c = 3.556(3)$ Å, and $\beta = 92.944(6)^\circ$, exhibit good agreement with the data obtained by the least-squares method reported by Kusachi et al. (1998). The atomic coordinates and selected bond distances for parasibirskite are listed in Tables 1 and 2, respectively. The crystallographic data of both minerals are compared in Table 3. A clinographic view of the refined structure is

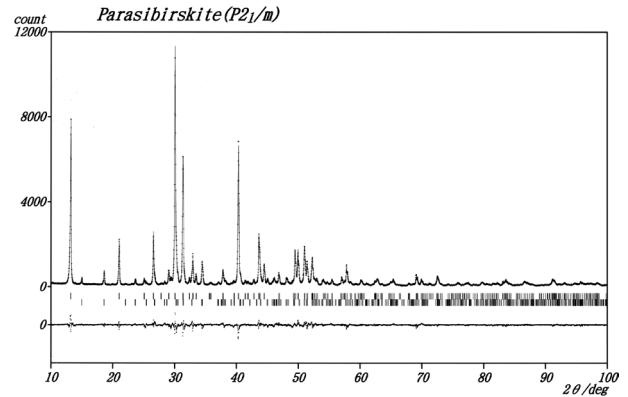


Figure 1. Rietveld refinement of parasibirskite structure. The black curves and dots indicate the observed data; the solid line, the calculated pattern; and the vertical marks, the possible Bragg reflections for parasibirskite (upper) and sibirskite (lower). The lower trace indicates the difference between the observed and the calculated patterns.

Table 1. Atomic coordinates of parasibirskite

		<i>x</i>	<i>y</i>	<i>z</i>	<i>Beq</i>
Ca	2e	0.147(1)	0.250	0.252(1)	1.48(5)
B	2e	0.716(1)	0.250	0.280(2)	0.9(2)
O1	2e	0.523(1)	0.250	0.367(1)	1.37(7)
O2	4f	0.819(1)	0.030(1)	0.240(1)	1.37(7)

Table 2. Selected interatomic distances (Å)

CaO ₆ Octahedra		BO ₃ Triangle	
Ca - O1	2.539(8)	B - O1	1.350(8)
- O2	2.509(3) × 2	- O2	1.395(5) × 2
- O2	2.363(3) × 2	Average	1.380
- O2	2.336(3) × 2		
Average	2.422		

Table 3. Crystallographic and physical properties of sibirskite and parasibirskite from Fuka

	Sibirskite ¹	Parasibirskite ²
Chemical formula	CaHBO ₃	CaHBO ₃
Space Group	<i>P2₁/a</i>	<i>P2₁/m</i>
Cell Constants		
<i>a</i>	8.643(6)	6.722(4)
<i>b</i>	9.523(2)	5.437(2)
<i>c</i>	3.567(3)	3.555(2)
β	119.23	93.00(5)
<i>V</i>	256.2(3)	129.8(2)
<i>Z</i>	4	2
<i>D</i> _{calc}	2.59	2.54
Vickers Hardness	339	121
Cleavage	---	(100)

¹ Kusachi et al. (1997).

² Kusachi et al. (1998).

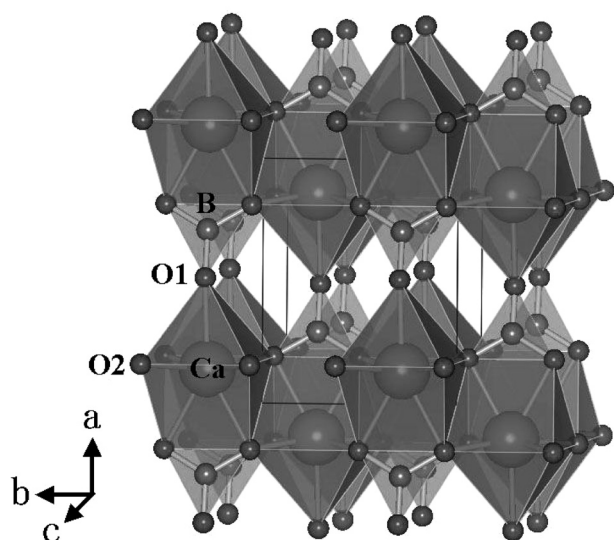


Figure 2. Crystal structure of parasibirskite. The structure consists of an edge-sharing CaO_7 polyhedron and BO_3 triangles. This figure was prepared using VICS-II. (Momma and Izumi, 2006).

shown in Figure 2.

DISCUSSION

The Rietveld refinement of parasibirskite confirmed the crystal structure model obtained by the Monte Carlo simulation based on the set of d -values and the intensity data. The unit cell consists of independent calcium and boron atoms and two independent oxygen atoms. Four oxygen atoms surround a calcium atom in a square coordination. One oxygen atom occupies the apical point of the square oxygen to form a distorted pyramid. On the other side of the square oxygen atoms, two oxygen atoms form a gable roof. The CaO_7 coordination in a monocapped distorted trigonal prism arrangement observed in the $2\text{CaO} \cdot \text{B}_2\text{O}_3$ structure (Ji et al., 1993; Schuckmann, 1969) is similar to

Table 4. Bond-valence sum of parasibirskite

	Ca	B	H*	Sum
O1	0.213	1.058	0.927 0.073	2.271
O2	0.231×2 0.343×2 0.369×2	0.937×2		1.880
Sum	2.099	2.932	1.000	6.031

* Hydrogen atom is assumed to connect with O1 atom.

the CaO_7 found in the parasibirskite structure. Symmetrically identical CaO_7 polyhedra in an edge-sharing arrangement form a layer structure extending along the b - and c -directions. The CaO_7 alternately direct up and down. The average Ca-O distance of parasibirskite is 2.422 Å, which is larger than that of sibirskite (2.366 Å, Miura and Kusachi, 2008). This may reflect the large coordination number of the calcium atom and the less dense structure of parasibirskite relative to that of sibirskite (Table 3). Parasibirskite is a dimorph of sibirskite that consists of CaO_6 double chains connected by BO_3 triangles. In contrast, parasibirskite consists of edge-shared CaO_7 layers connected by BO_3 triangles.

A boron atom shares one vertical oxygen atom of the CaO_7 polyhedron and two oxygen atoms of another CaO_7 in the neighboring layer. These CaO_7 layers connected by BO_3 triangles constitute the parasibirskite structure (Figure 2). The difference between the bond strengths normal and parallel to the layer reflects the cleavage of (100).

The O2 site, coordinated with three calcium atoms and one boron atom, satisfies the electrostatic bond valence. However, the O1 atom, surrounded by one calcium atom and one boron atom, does not satisfy the electrostatic bond valence requirement if the hydrogen atom is not taken into account. Therefore, the hydrogen atoms must be connected to the O1 site. The bond valence calcula-

Table 5. Coordination numbers and structure of calcium borate minerals from Fuka

Mineral	Formula	Ca ¹	B ²	Arrangements of Ca polyhedron	References ³
Takedaite	$3\text{CaO} \cdot \text{B}_2\text{O}_3$	8	3	Screw arrangement of $[\text{CaO}_8]$	(a)
Sibirskite	$2\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$	6	3	Double chain of $[\text{CaO}_6]$ connected by $[\text{BO}_3]$	(b)
Parasibirskite	$2\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$	7	3	Sheet structure of $[\text{CaO}_7]$ connected by $[\text{BO}_3]$	(c)
Uralborite	$\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	8	4	$[\text{CaO}_8]$ ring structure	(d)
Nifontovite	$3\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$	8	4	$[\text{CaO}_8]$ single chains connected by $3[\text{BO}_4]$	(e)
Olshanskite	$3\text{CaO} \cdot 2\text{B}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$	8	4	Ring structure of $[\text{CaO}_8]$	(f)
Frolovite	$\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	8	4	$[\text{CaO}_8]$ connected by $2[\text{BO}_4]$	(g)
Pentahydroborite	$\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	7	4	Independent $[\text{CaO}_7] + 2[\text{BO}_4]$	(h)

¹ Coordination number of calcium.

² Coordination number of boron.

³ References: (a), Vegas et al. (1975); (b), Miura and Kusachi, (2008); (c), This study; (d), Simonov et al. (1977); (e), Simonov et al. (1978); (f), Callegari et al. (2001); (g), Egorov-Tismenko et al. (1972); (h), Kazanskaya et al. (1977).

tions (Brese and O'Keeffe, 1991; Brown, 2002) confirmed this structure model (Table 4).

Calcium borate hydroxide minerals in the CaO-B₂O₃-H₂O system observed in Fuka change their physical properties such as density and hardness as a function of H₂O content (Kusachi et al., 1999). The coordination number of boron also changes as a function of H₂O content. The BO₃ triangle is observed in minerals in which the H₂O content is relatively low, such as takedaite (Ca₂B₂O₅) and sibirskite (CaHBO₃). Other calcium borate hydroxide minerals, which have more H₂O content than sibirskite, form a BO₄ tetrahedron in their structure (Table 5). The BO₃ triangle in the parasibirskite structure exhibits this characteristic. The change in the coordination number of the boron atom as a function of H₂O content is required to compensate the reduction in the valence of oxygen produced by the incorporation of the hydrogen atom.

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