LETTER

Crystal structure of sibirskite (CaHBO₃) by Monte Carlo simulation and Rietveld refinement

Hiroyuki MIURA* and Isao KUSACHI**

Department of Natural History Sciences, Graduate School of Science, Hokkaido University, Sapporo 060–0810, Japan *Department of Earth Sciences, Faculty of Education, Okayama University, Okayama 700–8530, Japan

The crystal structure of sibirskite (CaHBO₃) was solved by the Monte Carlo simulation using powder X-ray diffraction data and confirmed by the Rietveld refinement. The mineral sibirskite is monoclinic with space group $P2_1/a$ and cell constants of a = 8.643(6), b = 9.523(2), c = 3.567(3) Å, and $\beta = 119.23(3)^\circ$. The unit cell consists of independent atoms such as calcium, boron, hydrogen, and three oxygen atoms. The calcium atom is surrounded by six oxygen atoms in an octahedral coordination, and a symmetrical pair of edge-shared CaO₆ octahedra forming a double chain elongates the crystallographic c axis. The CaO₆ double chains are not directly connected to each other. The BO₃ triangles are linked to one vertical and two shared oxygen atoms in three CaO₆ double chains to form the sibirskite structure. Sibirskite is isostructural with nahcolite (NaHCO₃), which consists of NaO₆ double chains and CO₃ triangles.

Keywords: Sibirskite, CaHBO₃, Nahcolite, Crystal structure, Monte Carlo simulation

INTRODUCTION

The mineral sibirskite (CaHBO₃) was first discovered in the eastern Siberian Yuliya Svintsoviya deposit and the Novofrolovskoye B-Cu deposit in the Urals (Vasilkova, 1962). More recently, a third occurrence of sibirskite was discovered in Fuka, Okayama, Japan, and the chemical composition, cell constants, and powder X-ray diffraction data were reported for the Japanese sample (Kusachi et al., 1997). However, the crystal structure of sibirskite has not been determined due to the lack of single-crystal specimens suitable for structural analysis. In the present study, the Monte-Carlo-based simulation developed by Miura and Kikuchi (1999) is employed to solve an initial model for the crystal structure of sibirskite using a set of d values and intensity data reported by Kusachi et al. (1997). Further, the crystal structure is refined by the Rietveld method.

STRUCTURAL ANALYSIS

The crystal data for sibirskite provided by Kusachi et al.

doi:10.2465/jmps.071022g H.Miura, hiro@sci.hokudai.ac.jp Corresponding author I.Kusachi, kusachi@cc.okayama-u.ac.jp (1997) are as follows: the chemical formula is CaHBO₃ (Z = 4); the cell constants are a = 8.643(6), b = 9.523(2),c = 3.567(3) Å, and $\beta = 119.23(3)^{\circ}$; and the space group is $P2_1/a$. The X-ray powder diffraction (XRD) data for sibiriskite were also provided by Kusachi et al. (1997). The coordinates of the calcium, boron, and oxygen atoms are determined by the Structure Model-Assembly Program developed by Miura and Kikuchi (1999) 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 coordinates of the hydrogen atoms cannot be determined. The four calcium atoms in the unit cell must be located in pairs of the following Wyckoff positions: 2a, 2b, 2c, 2d or one general equivalent position 4e. In the preliminary calculation, all the possible combinations of four calcium, four boron, and twelve oxygen atoms in the unit cell were tested. The search program could not determine suitable arrangements in which four calcium atoms and four oxygen atoms are located in 2a-2d positions since the interatomic distances are smaller than the sum of their ionic radii. The structure model in which four calcium atoms are located in 2a-2d positions gives R = 0.285; however, the structural arrangement was not reasonable because the calcium atom was inaccurately coordinated with the oxy-

h	k	l	dcalc. ^a	<i>I</i> obs.	Icalc.	h	k	l	dcalc. ^a	<i>I</i> obs.	Icalc.
1	1	0	5.913	33	32	-1	2	2	1.599	1	1
0	2	0	4.762	29	27	-4	4	1	1.592	3	2
1	2	0	4.026	4	3	0	6	0	1.587	3	3
2	0	0	3.771	36	35	3	1	1	1.586	8	8
2	1	0	3.506	11	10	-4	2	2	1.571	1	1
-1	1	1	3.329	14	15	-3	5	1	1.557	3	2
-2	0	1	3.327	21	22	0	0	2	1.556	2	2
-2	1	1	3.141	14	16	0	1	2	1.536	5	5
0	0	1	3.113	1	1	2	4	1	1.519	3	3
0	1	1	2.959	72	71	-5	3	1	1.518	1	1
2	2	0	2.956	81	80	3	5	0	1.518	2	2
1	3	0	2.926	16	16	1	5	1	1.511	1	1
-2	2	1	2.727	33	34	-5	1	2	1.495	2	2
0	2	1	2.606	100	100	5	1	0	1.489	2	2
-3	1	1	2.603	6	6	0	2	2	1.479	4	4
3	1	0	2.430	8	9	4	4	0	1.478	1	1
2	3	0	2.429	1	1	2	6	0	1.463	3	3
1	1	1	2.401	2	2	-5	2	2	1.443	1	1
0	4	0	2.381	1	1	-2	6	1	1.433	2	2
-3	2	1	2.352	14	14	-2	4	2	1.424	1	1
3	2	0	2.223	25	24	0	6	1	1.414	1	1
0	3	1	2.222	1	1	-3	6	1	1.369	1	1
-4	0	1	2.141	4	3	-5	3	2	1.367	3	3
-4	1	1	2.089	2	2	5	3	0	1.363	4	4
-3	3	1	2.059	20	21	4	5	0	1.340	1	1
2	4	0	2.013	10	10	-6	1	2	1.339	1	1
-1	4	1	1.978	5	5	1	6	1	1.337	1	1
2	0	1	1.974	14	15	0	4	2	1.303	2	1
3	3	0	1.971	10	11	4	2	1	1.297	1	1
-4	2	1	1.953	5	6	2	7	0	1.280	1	1
-2	4	1	1.936	16	17	6	0	0	1.257	1	1
0	4	1	1.891	21	22	-7	1	1	1.209	2	2
4	0	0	1.886	2	2	2	2	2	1.201	1	1
1	5	0	1.847	2	2	-7	1	2	1.193	1	1
2	2	1	1.823	10	8	0	8	0	1.191	1	1
-3	4	1	1.787	1	1	-5	5	2	1.185	1	1
-2	0	2	1.777	13	11	5	5	0	1.183	2	2
4	2	0	1.753	4	4	-4	6	2	1.149	1	1
-3	1	2	1.734	11	11	5	1	1	1.146	1	1
-5	1	1	1.701	14	14	-7	3	2	1.124	1	1
-1	5	1	1.679	2	2	-2	2	3	1.122	1	1
-1	1	2	1.671	1	1	0	6	2	1.111	1	1
-4	0	2	1.664	2	3	-3	3	3	1.110	1	1
-2	2	2	1.665	3	3	7	1	0	1.071	1	1
0	5	1	1.625	1	1	-5	7	1	1.069	1	1

Table 1. X-ray diffraction data of sibirskite obtained from Rietveld refinement

^a Based on *a*=8.643(6), *b*=9.523(2), *c*=3.567(3) Å, β=119.23(3)°

gen atoms. Arrangement of all the atoms in the general equivalent position (4e) affords better *R* values ($R = \Sigma |I_{obs} - I_{calc}| / \Sigma I_{obs}$) in the Monte Carlo simulation than in the other combinations of Wyckoff positions. The struc ture model in which all independent atoms are located at the 4e position was selected as the initial model.

The search procedures established by Miura et al. (2000) have been used for the present structural analysis.

The obtained model displays the edge-shared CaO_6 double chain extending along the *c* axis and the BO₃ triangle linked to one vertical and two shared oxygen atoms in three CaO_6 double chains. Since the positions of the boron atom did not converge to a specific site, it was not possible to determine a suitable position for the boron atom from the set of *d* values and intensity data. This may be due to both the relatively low scattering factor of boron



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

and the fixation of temperature factors (1.0) for all the atoms required to reduce the calculation time. However, it is expected that the boron atoms will be located at the center of the oxygen triangles present in the model of sibirskite to form the BO₃ triangles, which is common for borate minerals such as takedaite $[Ca_3(BO_3)_2;$ Schuckmann, 1969; Vegas et al., 1975] and sassolite (H₃BO₃; Gajhede et al., 1986). The *R* value for the final simulated structure is 0.243.

STRUCTURE REFINEMENT

The powder XRD pattern of the Japanese sibirskite sample, which was mounted on a silicon non-reflection specimen holder, was collected using a Mac Science MX-Labo diffractometer with Cu-K α radiation (40 kV, 30 mA, 0.5°-0.5°-0.15 mm slit) in a step scanning mode over a 2 θ range of 10°-100° in increments of 0.02° (20 seconds/ step). The intensities of the XRD peaks were measured after monochromatization using pyrolytic graphite for the Rietveld refinement. The XRD pattern thus determined includes almost all the peaks attributed to sibirskite and calcite and several weak peaks due to unknown minerals.

The program RIETAN-2000 (Izumi and Ikeda, 2000) was used for the Rietveld refinement. The crystal structures of sibirskite and calcite were refined simultaneously. The structure model obtained by employing the abovementioned Monte Carlo search was used as the initial sibirskite structure. The 2θ region of 16.5° - 17.5° in which an unknown peak was present was excluded from the calculation. Since the maximum B-O distance of the BO₃ triangles in borate minerals is 1.403 Å (Howthorne et al., 1996), all the B-O distances in the sibirskite structure



Figure 2. Crystal structures of sibirskite and nahcolite. (A) sibirskite (CaHBO₃) and (B) nahcolite (NaHCO₃, Sass and Scheuerman, 1962). Hydrogen coordinations in both minerals are specified by the bond valence calculation (Brown, 2002). The figures were prepared using VICS-II. (Monma and Izumi, 2006).

were properly restricted to less than 1.40 Å to avoid the distortion of the BO₃ triangle. The background parameters, peak shift parameters, profile parameters, cell constants, atomic coordinates, and anisotropic temperature factors were optimized in the calculation. The final *R* values for pattern fitting are $R_{wp} = 7.75$ and $R_p = 5.93\%$. The *R* values based on the intensity and structure factors are $R_I = 4.22\%$ and $R_F = 4.68\%$ for sibirskite, and $R_I = 7.51\%$ and $R_F = 4.22\%$ for calcite. The results of the Rietveld refinement are shown in Table 1 and Figure 1, and the crystal structure projected onto the (001) plane is shown in Figure 2, along with the crystal structure of nahcolite (NaHCO₃; Sass and Scheuerman, 1962). The atomic coordinates and selected bond distances are listed in Tables 2 and 3, respectively.

DISCUSSION

The Rietveld refinement of sibirskite confirmed the crystal structure obtained by the Monte Carlo simulation based on the set of d values and the intensity data reported

		x	У	Ζ	Beq
Ca	4e	0.213(1)	-0.007(1)	0.508(1)	5.30
В	4e	0.574(1)	0.236(1)	-0.138(2)	2.00
01	4e	0.076(1)	0.118(1)	0.829(2)	4.92
02	4e	0.708(1)	0.147(1)	0.896(1)	3.42
03	4e	0.428(1)	0.174(1)	-0.135(1)	6.54

Table 2. Atomic coordinates of sibirskite

Table 1 Bond-valence sum of sibirskite

	rable in Boli	a valence ban		
	Ca	В	H*	Sum
01	0.289	0.953		1.898
	0.364			
	0.292			
02	0.403	0.942	0.189	1.927
02	0 393	0.9.12	01107	
	0.575			
03	0.319	0.942	0.811	2.072
Sum	2.060	2.837	1.000	5.897
the second se				

* Hydrogen atom located at 1.03Å from O3 satisfies the requirement for bond valence sum of O2 and O3 (Brese and O'Keeffe, 1991)

by Kusachi et al. (1997). The unit cell thus determined consists of independent calcium and boron atoms and three independent oxygen atoms. The calcium atom is surrounded by six oxygen atoms in an octahedral coordination. A pair of symmetrically identical CaO₆ octahedra in an edge-sharing arrangement present in their edgeshared chain to form a double chain elongated along the c axis. The abovementioned analogous double chains with a pair of symmetrically identical MgO₆ octahedra in an edge-sharing arrangement are found in szaibelyite {Mg₂ (OH)[B₂O₄(OH)]; Takeuchi and Kudoh, 1975} connected directly to each other by corner-sharing oxygen atoms. On the other hand, the CaO₆ double chains in sibirskite are not directly connected to each other. The BO₃ triangles are linked to one vertical and two shared oxygen atoms in three CaO₆ double chains to form the sibirskite structure (Fig. 2).

The hydrogen site could not be determined by the X-ray diffraction analysis. The O1 atom is surrounded by three calcium atoms and one boron atom, thereby satisfying the electrostatic bond valence requirement (Table 3). However, the O2 site is coordinated with two calcium atoms and one boron atom, while the O3 site is coordinated with one calcium atom and one boron atom. These two sites do not satisfy the bond valence requirements, and therefore the hydrogen atoms must be connected to either

Table 3. Selected interatomic distances (Å)

CaO ₆	Octahedra	BO ₃	Triangle
Ca - O1	2.426(8)	B - O1	1.389(14)*
- 01	2.341(4)	- O2	1.393(13)*
- 01	2.423(4)	- O3	1.393(14)*
- 02	2.303(4)	Average	1.392
- 02	2.312(5)		
- O3	2.390(5)		
Average	2.366		

* B-O distances are restricted to less than 1.40 Å (Hawthorne et al., 1996)

Table 5.	Bond-valence su	im of nahcolite
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	Na	С	H*	Sum
01	0.165	1.406		1.945
	0.179			
	0.195			
02	0.186	1.410	0.188	1.989
	0.205			
03	0.184	1.126	0.812	2.122
Sum	1.114	3.942	1.000	6.056

* Hydrogen atom located at 1.03Å from O3 satisfies the requirement for bond valence sum of O2 and O3 (Brese and O'Keeffe, 1991)

site. The bond valence calculations (Brese and O'Keeffe, 1991; Brown, 2002) are carried out to determine which oxygen atom has a covalent bond with the hydrogen atoms. The bond valence sum of the structure model for sibirskite and nahcolite are shown in Tables 4 and 5, respectively, for comparison. It is likely that one hydrogen atom satisfies the requirement for the bond valence sum of O2 and O3 atoms in both structures. The structure of sibirskite is similar to that of nahcolite, which validates the sibirskite structure model.

Parasibirskite (CaHBO₃), discovered at Fuka, Japan (Kusachi et al., 1998), is a dimorph of sibirskite, being unknown in terms of crystal structure. The topological relationship between the sibirskite (CaHBO₃) structure and the szaibelyite { $Mg_2(OH)[B_2O_4(OH)] = 2[MgHBO_3]$ } structure will help to determine the crystal structure of parasibirskite.

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