# Shimazakiite-4*M* and shimazakiite-4*O*, $Ca_2B_2O_5$ , two polytypes of a new mineral from Fuka, Okayama Prefecture, Japan

I. KUSACHI<sup>1,2</sup>, S. KOBAYASHI<sup>3</sup>, Y. TAKECHI<sup>4</sup>, Y. NAKAMUTA<sup>5</sup>, T. NAGASE<sup>6</sup>, K. YOKOYAMA<sup>2</sup>, K. MOMMA<sup>2</sup>, R. MIYAWAKI<sup>2,\*</sup>, M. SHIGEOKA<sup>2</sup> AND S. MATSUBARA<sup>2</sup>

<sup>1</sup> Department of Earth Sciences, Faculty of Education, Okayama University, Okayama 700-8530, Japan

<sup>2</sup> Department of Geology and Palaeontology, National Museum of Nature and Science, Tsukuba 305-0005, Japan

<sup>3</sup> Department of Applied Science, Faculty of Science, Okayama University of Science, Okayama 700-0005, Japan

<sup>4</sup> Kurashiki Museum of Natural History, Kurasiki 710-0046, Japan

<sup>5</sup> Kyushu University Museum, Fukuoka 812-8581, Japan

<sup>6</sup> Tohoku University Museum, Sendai 980-8578, Japan

[Received 28 February 2012; Accepted 13 December 2012; Associate Editor: Allan Pring]

## ABSTRACT

Shimazakiite occurs as greyish white aggregates up to 3 mm in diameter. Two polytypes, shimazakiite-4M and shimazakiite-4O, have been identified, the former in nanometre-sized twin lamellae and the latter in micrometre-sized lamellae. Shimazakiite was discovered in an irregular vein in crystalline limestone near gehlenite-spurrite skarns at Fuka mine, Okayama Prefecture, Japan. Associated minerals include takedaite, sibirskite, olshanskyite, parasibirskite, nifontovite, calcite and an uncharacterized hydrous calcium borate. The mineral is biaxial (-), with the following refractive indices (at 589 nm):  $\alpha = 1.586(2)$ ,  $\beta = 1.650(2)$ ,  $\gamma = 1.667(2)$  and  $2V_{calc} = 53^{\circ}$  [shimazakiite-4M]; and  $\alpha = 1.584(2), \beta = 1.648(2), \gamma = 1.670(2)$  and  $2V_{calc} = 54.88^{\circ}$  [shimazakiite-40]. Quantitative electronmicroprobe analyses (means of 28 and 25 determinations) gave the empirical formulae  $Ca_2B_{1,92}O_{4,76}(OH)_{0,24}$  and  $Ca_2B_{1,92}O_{4,76}(OH)_{0,24}$  for shimazakiite-4M and shimazakiite-4O, respectively. The crystal structure refinements:  $P2_1/c$ , a = 3.5485(12), b = 6.352(2), c = 19.254(6) Å,  $\beta =$ 92.393(13)°, V = 433.6(3) Å<sup>3</sup> [for shimazakiite-4*M*]; and  $P2_12_12_1$ , a = 3.55645(8), b = 6.35194(15), c = 100019.2534(5) Å, V = 434.941(18) Å<sup>3</sup>[for shimazakiite-40], converged into  $R_1$  indices of 0.1273 and 0.0142, respectively. The crystal structure of shimazakiite consists of a layer containing  $B_2O_5$  units (two near-coplanar triangular corner-sharing BO<sub>3</sub> groups) and 6- and 7-coordinate Ca atoms. Different sequences in the c direction of four layers are observed in the polytypes. The five strongest lines in the powder-diffraction pattern [listed as d in Å(I)(hkl)] are: 3.02(84)(022); 2.92(100)(104); 2.81(56)(104); 2.76(32)(113);  $1.880(32)(11\overline{8}, 12\overline{6}, 126, 118)$  [for shimazakiite-4M]; and 3.84(33)(014); 3.02(42)(022); 2.86(100)(104); 2.79(29)(113); 1.903(44)(126,118) [for shimazakiite-40].

**KEYWORDS:** shimazakiite, new mineral, calcium borate, Fuka, skarn.

#### Introduction

A calcium borate mineral, with a composition different from any known mineral species, was recognized by the first author in skarn from Fuka

\* E-mail: miyawaki@kahaku.go.jp DOI: 10.1180/minmag.2013.077.1.09 mine, Okayama Prefecture, Japan. It has a composition between takedaite,  $Ca_3B_2O_6$  (Kusachi *et al.*, 1995); calciborite,  $CaB_2O_4$  (Petrova, 1955); and sibirskite (Vasilkova, 1962) and parasibirskite (Kusachi *et al.*, 1998), both CaHBO<sub>3</sub>, and is distinct from any previously described synthetic  $Ca_2B_2O_5$  phase. The mineral has been named shimazakiite in honour of

Hidehiko Shimazaki (b. 1939), Emeritus Professor at the University of Tokyo, in recognition of his outstanding contribution to skarn mineralogy (e.g. Shimazaki and Ozawa, 1978; Shimazaki, 1980). The mineral data and name (IMA 2010-085a) have been approved by the International Mineralogical Association, Commission on New Minerals, Nomenclature and Classification. The type specimen of shimazakiite has been deposited in the collections of the National Museum of Nature and Science, Tokyo, Japan, under registration number NSM-M41025.

## Occurrence

Shimazakiite is found as aggregates up to 3 mm in diameter, which are made up of nanometre-sized (Fig. 1) to micrometre-sized lamellae. At least two polytypes, shimazakiite-4*M* and shimaza-kiite-4*O*, are present in these aggregates. Shimazakiite-4*M* tends to occur in nanometre-sized twin lamellae and shimazakiite-4*O* in micrometre-sized lamellae. Shimazakiite occurs in crystalline limestone near gehlenite-spurrite skarns at Fuka mine, Okayama Prefecture, Japan

(34°46′N, 133°26′E). It is closely associated with takedaite and calcite, which both formed during the post-metasomatic stage of primary skarn mineralization. Associated minerals include sibirskite, parasibirskite, olshanskyite, nifontovite (Kusachi and Henmi, 1994) and an uncharacterized hydrous calcium borate. Gehlenite and spurrite occur as pyrometasomatic alteration products of the limestone.

The characterizations of the specified polytypes of shimazakiite were carried out using data from two specimens. The data for shimazakiite-4*M* were obtained from nanometre-sized twin lamellae on specimen NSM-M41025 (the type specimen). Those for shimazakiite-4*O* were obtained from micrometre-sized lamellae on a specimen from the same collecting area, registration number NSM-M43418.

The micro-texture of shimazakiite was characterized by polarized-light microscopy and transmission electron microscopy (TEM). For TEM observations, thin foils were removed from petrographic thin sections and prepared using the argon ion-thinning method, with a liquid nitrogen cooling system. The TEM



FIG. 1. Photomicrographs of shimazakiite-4*M* characterized by lamellar twinning between crossed polars; the field of view is  $\sim 0.9 \times 1.2$  mm. Most of the granular crystals without twinning are takedaite or calcite.

# SHIMAZAKIITE-4M AND SHIMAZAKIITE-4O: CA2B2O5 POLYTYPES



FIG. 2. A TEM image of shimazakiite-4*M*. The crystal includes numerous planar defects parallel to (001). The thickness of the lamellae is on the nanometre scale and the sequence of the planar faults is random.

Constituent		– Shimaz	akiite-4 <i>M</i> –		– Shimaz	akiite-40 –	Probe
	(wt	.%)	Range	(w	t.%)	Range	standard
CaO	61.09	9(25)	60.51-61.46	61.3	30(17)	60.85-61.50	Takedaite
$B_2O_3$	36.39	9(76)	34.61-37.76	36.5	51(40)	35.61-37.35	Takedaite
H <sub>2</sub> O	2.52*	1.19 <sup>†</sup>		2.19*	1.20 <sup>†</sup>		
Total	100	98.67		100	99.01		

\* Water content by difference.

<sup>†</sup> Water content re-calculated based on the stoichiometry  $Ca_2B_{2-x}O_{5-3x}(OH)_{3x}$ .

4M.	
ızakiite-	
shime	
for	
data	
diffraction	
X-ray	
2a.	
TABLE	
-	

ABI	- E						
Ч	k	1	$I_{\rm obs}$	$d_{\rm obs}$	$d_{\mathrm{calc}}^{*}$	$d_{\rm calc}^{**}$	$I_{\rm calc}^{**}$
0	0	2	Э	9.63	9.62	9.63	3
0	-	1	19	6.03	6.03	6.03	13
0	-	2	7	5.30	5.30	5.30	4
0	-	4	33	3.84	3.84	3.84	19
-	0	1	7	3.50	3.49	3.50	7
0	-	S	24	3.29	3.29	3.29	15
0	0	9	5	3.21	3.21	3.21	З
-	0	Э	19	3.11	3.11	3.11	18
0	2	5	42	3.02	3.02	3.02	55
-	-	2	8	2.95	2.95	2.95	S
-	0	4	100	2.86	2.86	2.86	100
-	-	З	29	2.79	2.79	2.79	28
-	-	4	11	2.61	2.61	2.61	6
0	-	2	4	2.53	2.52	2.52	ю
0	2	S	11	2.45	2.45	2.45	6
0	0	×	5	2.41	2.41	2.41	2
-	2	0	ŝ	2.37	2.37	2.37	2
-	2	2	12	2.30	2.30	2.30	13
0	-	~	10	2.25	2.25	2.25	5
-	-	9	22	2.23	2.23	2.23	22
0	З	1	9	2.11	2.10	2.10	6
0	З	2	12	2.07	2.07	2.07	14
0	З	ŝ	5	2.01	2.01	2.01	З
1	0	8	8	1.992	1.992	1.993	9
0	З	4	2	1.936	1.938	1.938	2
-	0	9	) 44	1 903	1.905	1.906	32
_	_	×	;	CO/-1	1.901	1.902	23
0	ŝ	S	4	1.852	1.855	1.855	Э
0		10	10	1.842	1.842	1.843	9
-	Э	1	7	1.810	1.811	1.811	7
-	ŝ	2	15	1.787	1.787	1.788	12
0	0	0	17	1.776	1.777	1.778	11
0	-	-	0	1 706	( 1.704	1.706	4
-	З	4	ہ ~	1./00	1.701	1.702	4
-	2	×	11	1.687	1.688	1.688	9
2	0	4	2	1.667	1.667	1.668	-
0,	20	0 ,	12	1 645	1.646	1.646	9 1
-	c	ŝ	1	210-1	1.644	1.645	2

	$I_{\rm obs}$	~	$d_{\rm obs}$	$d_{\mathrm{calc}}^{*}$	$d_{\rm calc}^{**}$	$I_{\rm calc}^{**}$
				9.60	9.62	4
	27		6.03	6.03	6.03	18
	14		5.31	5.30	5.30	S
	30		3.84	3.83	3.83	24
				3.55	3.55	4
_				3.29	3.28	4
~	19		3.30	3.29	3.29	18
				3.20	3.21	С
				3.14	3.13	С
				3.08	3.07	ŝ
				3.04	3.04	4
	84		3.02	3.02	3.02	68
	10(	0	2.92	2.91	2.91	100
_	Ċ			2.85	2.85	8
~	17		2.84	2.83	2.83	9
	56		2.81	2.80	2.80	48
	32		2.76	2.75	2.75	29
				2.64	2.65	S
				2.57	2.56	8
				2.52	2.52	4
	17		2.44	2.45	2.45	11
				2.40	2.40	б
				2.36	2.36	4
	16		2.31	2.33	2.33	4
			~	2.29	2.28	9
~	16		2.27	2.26	2.27	11
_			_	2.24	2.25	9
	19		2.19	2.19	2.19	17
-	6	-	~ ~ ~ ~	2.11	2.10	13
$\sim$	19	_	2.10	2.10	2.10	4
	23		2.07	2.07	2.07	17
-	0	-	~	2.02	2.03	б
$\sim$	10		7.01	2.01	2.01	4
				1.954	1.953	4
				1.938	1.938	0
_			_	1.928	1.934	14
-	27		1 000	1.927	1.929	20
_	70		1.000	1.881	1.879	20
_			[	1.868	1.866	14

I. KUSACHI ET AL.

s of refined lattice parameters from the powder XRD data;	0), $b = 6.3509(15)$ , $c = 19.248(4)$ Å, $V = 434.41(19)$ Å <sup>3</sup> .	asis of refined lattice parameters from the single-crystal	= 3.55645(8), b = 6.35194(15), c = 19.2534(5) Å, V =	Å <sup>3</sup>
* On the basis of refined la	a = 3.5537(10), b = 6.350	** On the basis of refine	XRD data; $a = 3.55645(8)$	434.941(18)) Å <sup>3</sup> .

4	0	0	4	З	8	4	0	З	0	1	0	4	0	4	ŝ	З	0	-	0	З	0	-	00	10	1	0	0	1			0
1.613	1.590	1.588	1.556	1.547	1.532	1.525	1.505	1.477	1.454	1.432	1.388	1.375	1.358	1.357	1.348	1.322	1.280	1.256	1.254	1.200	1.182	1.181	1.149	1.133	1.132	1.125	1.123	1.122	1.097	1.097	1.095
1.612	1.589	1.587	1.555	1.546	1.531	1.524	1.505	1.476	1.453	1.432	1.388	1.375	1.358	1.357	1.348	1.322	1.279	1.255	1.253	1.200	1.182	1.181	1.148	1.132	1.132	1.125	1.123	1.122	1.097	1.097	1.095
	~	~			~	~							~	~							$\sim$	-	~~		~	_	~	_			
1.611	1 507	/00.1	1.555	1.546		050.1		1.475	1.452	1.432	1.387	1.375	1 256	0001	1.345	1.321	1.279	1.257	1.254	1.200	1 1 2 2	1.102	1.148		1.131		1.123				
4	~	4	9	4		11		0	0	4	7	5	v	n	4	З	З	S	5	7	٢	r	б		б		4				
	5	~			_	~							$\overline{}$	~							$\overline{}$	~	~		~	_	~	_			
4	$\infty$	6	12	-	2	11	6	4	∽	12	4	14	-	ŝ	0	10	10	6	9	6		9	6 ;	<u>,</u> 4	Ś	16	$\infty$	16	14		9
	З	2	-	2	$\sim$	-	$\mathfrak{c}$	$\sim$	-	2	4	0	З	4	ŝ	$\mathfrak{c}$	-	$\sim$	ŝ	4	4	Ś	ŝ	n —	4	2	ŝ	-	ŝ	ŝ	-
2	0	1	0	2	7	1	0	7	7	0	1	0	2	1	2	1	2	7	2	1	0	0	- 17	- ന	2	0	0	1	_	_	ŝ

~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~	0 4 0 1 0 4 0	ろうてうう うしょ	n – m v 8 v m m 0 v 0 0 m 0
1.855 1.841 1.818 1.818 1.816 1.793 1.790 1.779	1.773 1.773 1.769 1.707 1.707 1.710 1.667	1.663 1.657 1.657 1.645 1.630 1.630 1.630 1.603 1.603	1.589 1.589 1.589 1.537 1.520 1.499 1.455 1.455 1.455 1.374 1.353 1.353 1.353 1.352 1.123
1.855 1.837 1.819 1.815 1.808 1.794 1.784	1.775 1.775 1.770 1.770 1.708 1.707 1.667	1.665 1.657 1.657 1.632 1.632 1.632 1.629 1.599	1.589 1.589 1.588 1.588 1.551 1.538 1.522 1.522 1.523 1.523 1.523 1.533 1.12333 1.12333 1.123333 1.12333 1.12333 1.123333 1.123335 1.12
$\sim$		~	
1.816	1.775 1.710	1.665 1.616 1.606	1.589
19	25 16	19 16 16	17
<u> </u>		_	
$\circ$ 1 0 1 1 0 0 $\sim$ 0 0 $\sim$ 0 0 $\sim$ 0	1001 million 4 m	8 12 0 1 0 1 0 8 8 8 9 9 1 0 1 0 1 0 1 0 1 0 1 0 0 0 0 0 0 0	5 8 2 1 1 8 8 5 1 1 5 8 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
$\omega - \omega \omega \omega \omega - \omega$	- 0 0 0 - 0 m -	- 0 0 m 0 m 0	4 π - 0 0 - 0 0 π π γ 4
0 0 1 1 1 1 1 1 1	0 - 0 - 0 - 0 0 - 0	0 1 0 1 0 1 0 0	5055055-5000

\* On the basis of refined lattice parameters from the powder XRD data; a = 3.553(3), b = 6.356(5), c = 19.21(5) Å,  $\beta = 92.16(19)^{\circ}$ , V = 433.4(12) Å<sup>3</sup>. \*\* On the basis of refined lattice parameters from the single-crystal XRD data; a = 3.5485(12), b = 6.352(2), c = 19.254(6) Å,  $\beta = 92.393(13)^{\circ}$ , V = 433.6(3) Å<sup>3</sup>. observations were performed using a JEOL JEM-2010 transmission electron microscope, operating at an accelerating voltage of 200 kV.

The shimazakiite-4M specimen described herein consists of fine lamellae on (001) (Fig. 2), the individual lamellae are several hundred nanometres thick. A random sequence of the planar faults can be seen in TEM images.

#### Physical and optical properties

Macroscopically, shimazakiite is greyish white; it has a white streak. The crystals are transparent and have a vitreous lustre. Shimazakiite is brittle, with an uneven fracture and no discernable cleavage. It is optically biaxial (-), with refractive indices measured at 589 nm of  $\alpha$  = 1.586(2),  $\beta = 1.650(2)$ ,  $\gamma = 1.667(2)$  and  $2V_{calc} =$ 53° [for shimazakiite-4M]; and  $\alpha = 1.584(2)$ ,  $\beta =$ 1.648(2),  $\gamma = 1.670(2)$  and  $2V_{calc} = 54.88^{\circ}$  [for shimazakiite-40]. The mineral is not pleochroic or fluorescent. The mean Vickers microhardness values are 549 kg  $\mathrm{mm}^{-2}$  (ranging between 516 and 566 kg mm<sup>-2</sup>) [for shimazakiite-4M] and 598 kg mm<sup>-2</sup> (ranging between 480 and 701 kg mm<sup>-2</sup>) [for shimazakiite-40] under a load of 50 g, corresponding to  $\sim 4\frac{1}{2}$  on the Mohs' scale. The density of shimazakiite-40, measured by immersion in a heavy liquid (Clerici solution) is 2.81(2); that of shimazakiite-4M could not be measured as insufficient pure material was available. The calculated densities are 2.78 and

2.77 g cm<sup>-3</sup> for shimazakiite-4*M* and shimazakiite-4*O*, respectively, on the basis of the empirical formulae and unit cells refined from single-crystal X-ray diffraction data.

#### **Chemical composition**

The composition was determined using a JEOL JXA-8800M electron microprobe operating in wavelength-dispersive spectrometry (WDS) mode at 15 kV, 20 nA with a 5 µm beam diameter. Pure takedaite was used as a standard for Ca and B. The X-ray lines used in the analyses were  $BK\alpha$  (measured using a layered dispersion element) and CaKa (measured using a PET crystal). The line intensities were collected for 60 and 30 s at the peak position and background positions, respectively. The analytical error was 0.01 and 0.002%, corresponding to  $\pm 0.36$  and  $\pm 0.12$  wt.% for B<sub>2</sub>O<sub>3</sub> and CaO, respectively. The means of 28 [shimazakiite-4M] and 25 [shimazakiite-40] analyses are listed in Table 1. The H<sub>2</sub>O was not determined directly due to a lack of pure material and was estimated by difference. Infrared spectroscopy (see below) confirmed the presence of OH within the structure. The empirical formulae (based on 5 O a.p.f.u.) for shimazakiite-4M and shimazakiite-4O are  $Ca_2B_{1.92}$ O<sub>4.76</sub>(OH)<sub>0.24</sub> and Ca<sub>2</sub>B<sub>1.92</sub>O<sub>4.76</sub>(OH)<sub>0.24</sub>, respectively. Chemically, shimazakiite varies from compositions which have almost no H<sub>2</sub>O and no B deficiency (e.g. CaO 61.29, B<sub>2</sub>O<sub>3</sub> 37.76;



FIG. 3. The infrared spectrum of shimazakiite-4M.

## SHIMAZAKIITE-4M AND SHIMAZAKIITE-4O: CA2B2O5 POLYTYPES

subtotal 99.05 wt.% with Ca:B = 2:1.99), to compositions with a B deficiency and corresponding  $\rm H_2O$  (e.g. CaO 61.01,  $\rm B_2O_3$  34.61;

subtotal 95.62 wt.% with Ca:B = 2:1.83). The low analytical total for the B-deficient material suggests substitution of  $3(OH)^{-1}$  for  $(BO_3)^{3-}$ .

TABLE 3.	Crystal	data,	data	collection	and	refinement	details	for	shimazakiite.
	2								

	Shimazakiite-4M	Shimazakiite-40
Crystal dimension (mm)	$0.2 \times 0.1 \times 0.03$	$0.2 \times 0.1 \times 0.03$
Diffractometer	298 Rigaku VariMay/R avis RAPID	298 Rigaku VariMay/R avis RAPID
Crystal to detector distance (mm)	127 40	127 40
Readout nixel mode (mm)	0 100	0 100
Radiation	ΜοΚα	ΜοΚα
Lattice parameters	110110	110110
a (Å)	3.5485(12)	3.55645(8)
b (Å)	6.352(2)	6.35194(15)
c (Å)	19.254(6)	19.2534(5)
β(°)	92.393(13)	90
$V(A^3)$	433.6(3)	434.941(18)
Extinction rules	l = 2n for $h0l$ and $k = 2n$ for $0k0$	h = 2n for $h00$ , $k = 2n$ for $0k0$ and
		l = 2n for $00l$
Space group	$P2_{1}/c$	$P2_{1}2_{1}2_{1}$
Ζ	4	4
Formula	$Ca_2(B_2O_5)$	$Ca_2(B_2O_5)$
$D_{\text{calc}} (g \text{ cm}^{-3})$	2.78	2.77
$\mu$ (cm <sup>-1</sup> )	25.314	25.236
2θ range (°)	6-55	6-55
Total oscillation images	440	440
First sweep ω (°)	130.0-190.0 in 0.5 step	130.0-190.0 in 0.5 step
χ (°)	45.0	45.0
Φ (°)	0.0	0.0
exposure rate (s/°)	150	100
Second sweep ω (°)	0.0-160.0 in 0.5 step	0.0-160.0 in 0.5 step
χ (°)	45.0	45.0
φ (°)	180.0	180.0
exposure rate (s/°)	150	100
Index ranges	$-4 \leq h \leq 4$	$-4 \leq h \leq 4$
	$-8 \leq k \leq 8$	$-7 \leq h \leq 8$
	$-24 \leq l \leq 24$	$-24 \leqslant h \leqslant 24$
No. measured reflections	3855	4334
No. unique reflections	1005	1005
No. observed reflections $[I > 2\sigma(I)]$	843	995
R <sub>int</sub>	0.0625	0.0156
No. of variable parameters	4/	83
$R_1$ [ $I > 2\sigma(I)$ ], $R_1$ (all reflections)	0.1273, 0.1379	0.0142, 0.0144
$wR_2$ (all reflections)	0.3632	0.0667
weighting parameters, a, b	U.1, U	0.1, 0
Goodness of fit $E^{-3}$	1.440	0.6/4
Final $\Delta \rho_{min}$ (e A $$ )	-1.338	-0.250
Final $\Delta \rho_{max}$ (e A $$ )	2.844	0.311

$$\begin{split} R_1 &= \Sigma[|F_o| - |F_c|] / \Sigma |F_o| \\ wR_2 &= \{ \Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2] \}^{\frac{1}{2}} \\ w &= 1 / [\sigma^2(F_o^2) + (aP)^2 + bP] \\ P &= [2F_c^2 + F_o^2] / 3 \end{split}$$

	x/a	y/b	z/c	$U_{\rm eq}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Shimazak	iite-4 <i>M</i>									
Cal	0.2885(6)	0.9493(4)	0.21050(12)	0.0066(8)	0.0083(12)	0.0072(13)	0.0042(12)	-0.0006(8)	-0.0006(9)	0.0015(9)
Ca2	0.7533(6)	0.1956(4)	0.06186(12)	0.0066(8)	0.0075(13)	0.0075(13)	0.0046(12)	0.0002(8)	-0.0014(8)	0.0026(9)
81	0.169(4)	0.465(2)	0.1569(7)	$0.010(3)^{*}$						
B2	0.189(4)	0.253(2)	0.4170(7)	$0.009(3)^{*}$						
01	0.758(2)	0.8077(13)	0.0149(4)	0.0092(18)*						
02	0.771(2)	0.8908(12)	0.1336(4)	0.0056(16)*						
03	0.285(2)	0.2684(13)	0.1481(4)	0.0068(17)*						
04	0.972(3)	0.5495(15)	0.0971(5)	0.019(2)*						
05	0.203(2)	0.5761(13)	0.2171(4)	0.0074(17)*						
Shimazak	iite-40									
Cal	0.29761(12)	0.20104(5)	0.210507(15)	0.00757(14)	0.0082(2)	0.0072(2)	0.00734(19)	-0.00052(10)	0.00001(12)	-0.00008(14)
Ca2	0.79738(12)	0.44688(5)	0.061518(15)	0.00791(14)	0.0078(2)	0.0088(2)	0.0072(2)	-0.00019(11)	0.00014(12)	0.00011(12)
81	0.1863(5)	0.7181(3)	0.15670(9)	0.0079(4)	0.0061(8)	0.0090(8)	0.0084(7)	0.0026(5)	-0.0006(6)	-0.0011(8)
B2	0.1426(5)	0.5033(3)	0.41790(8)	0.0074(4)	0.0070(7)	0.0051(8)	0.0101(7)	-0.0007(6)	-0.0006(6)	0.0012(7)
01	0.7986(3)	0.05583(15)	0.01528(5)	0.0094(2)	0.0104(5)	0.0106(6)	0.0071(5)	0.0017(4)	-0.0002(4)	0.0011(6)
02	0.7950(4)	0.14306(17)	0.13453(6)	0.0091(3)	0.0093(6)	0.0098(5)	0.0082(5)	-0.0040(4)	-0.0011(5)	0.0021(5)
03	0.3157(4)	0.51855(18)	0.14809(6)	0.0105(3)	0.0117(6)	0.0093(5)	0.0105(5)	0.0019(4)	0.0014(5)	0.0030(6)
04 D	0.0037(4)	0.80046(16)	0.09633(5)	0.0114(3)	0.0198(6)	0.0071(5)	0.0072(5)	-0.0007(4)	-0.0030(5)	0.0036(6)
05	0.2079(4)	0.82822(16)	0.21757(6)	0.0097(3)	0.0123(6)	0.0091(6)	0.0078(5)	0.0002(4)	-0.0004(5)	-0.0012(5)

	for shimazakiite.
¢	
0	4
	parameters
	displacement
	and
	coordinates a
	atom
	Fractional
	4
	TABLE

\* These are  $U_{\rm iso.}$ 

100

I. KUSACHI ET AL.

Therefore, although the ideal endmember formula for shimazakiite is  $Ca_2B_2O_5$ , the formula taking into account the  $3(OH)^-$  for  $(BO_3)^{3-}$  substitution can be better written  $Ca_2B_{2-x}O_{5-3x}(OH)_{3x}$ , with x = 0-0.2. The amount of  $H_2O$  in shimazakiite, recalculated on the basis of this stoichiometry, is listed in Table 1 for comparison.

## Spectroscopy

The infrared absorption spectrum was measured in a KBr disc using a JEOL JIR6000 FTIR spectrometer. The spectrum has an OH-stretching band at 3440  $\text{cm}^{-1}$ , and bands in the region 1360-320 cm<sup>-1</sup>, which are due to the borate group (Fig. 3). No contamination by other hydrous and/or hydroxide mineral(s), such as sibirskite, parasibirskite, olshanskyite, nifontovite or the uncharacterized hydrous calcium borate, was found under the optical and electron microscope, or detected in the powder X-ray diffraction studies of the studied sample. As the very small shoulder at around 1600 cm<sup>-1</sup> is likely to be produced by H-O-H bending, which can be attributed to adsorbed water molecules, we can confirm that only OH is present in the structure of shimazakiite.

# Crystallography

The powder X-ray diffraction patterns for shimazakiite-4M and shimazakiite-4O were obtained using a Gandolfi camera with a diameter of 114.6 mm and Ni-filtered CuKa radiation. The data were recorded on an imaging plate, and processed with a Fuji BAS-2500 bio-image analyser using a computer program written by Nakamuta (1999). Powder X-ray diffraction data for the two polytypes of shimazakiite are listed in Table 2. The reflections in both patterns were indexed by reference to simulated patterns based on the structures determined by crystal structure analyses. The lattice parameters were refined with diffraction-angle data calibrated using an external Si-standard reference material (NBS 640b) using a computer program written by Toraya (1993).

Single crystals of shimazakiite-4M and shimazakiite-4O were picked from the thin sections that were analysed by electron microprobe, and were individually mounted on glass fibres. All measurements were made on a Rigaku R-AXIS RAPID curved imaging plate diffractometer using MoK $\alpha$  radiation monochromated and focussed by a VariMax confocal multilayer mirror. The lattice parameters and experimental conditions are summarized in Table 3. The data were empirically corrected for absorption, and for Lorentz and polarization effects.

The crystal structures of the two polytypes of shimazakiite were independently solved by the charge flipping method (Oszlánvi and Süto, 2004, 2005) using Superflip (Palatinus and Chapuis, 2007). Space group symmetries of  $P2_1/c$  and  $P2_12_12_1$ , which were the space groups suggested by extinctions in the single-crystal X-ray diffraction patterns, were determined from the symmetries of the electron densities calculated by Superflip. For both polytypes, all the atom positions were found by inspecting the electron density distributions. The deficiency of B atoms was ignored in the crystal-structure analyses and the Ca, B and O sites were fixed at full occupancy. The final cycle of full-matrix least-squares refinement (SHELXL97; Sheldrick, 2008) on  $F^2$ converged into  $R_1$  agreement indices of 0.1273 and 0.0142 for shimazakiite-4M and shimazakiite-40, respectively. Owing to the poor quality of the crystal of shimazakiite-4M, the final R value is relatively high, and refinement of anisotropicdisplacement parameters resulted in 'non positive definite' matrices for some B and O atoms. However, the structural model for shimazakiite-4M determined by this analysis is reasonable compared to the crystal structure of shimazakiite-40, which refined to a much more satisfactory Rvalue.

The final positional and displacement parameters are listed in Table 4. Selected interatomic distances and bond angles are summarized in Tables 5 and 6, respectively.

Selected area electron diffraction (SAED) patterns were obtained by TEM using a selected area aperture which limits the area producing the diffraction pattern to 400 nm in diameter. Figure 4 shows the  $<\overline{1}10>^*-c^*$  SAED pattern produced by shimazakiite-4M. There are diffuse streaks along [001]\*. The streaking indicates that the crystal has numerous planar faults caused by twinning on the composition plane (001). Possible twin laws are a mirror on (100) or a twofold axis about [001]. The streaking not visible in the  $b^*-c^*$  and  $c^*-<120>*$ SAED patterns. The electron diffraction patterns show no extinction rules for the 0k0 and 00l reflections, suggesting space groups P2, P2/m or Pm, however as dynamic (multiple) scattering occurs commonly in electron diffraction the SAED patterns are also consistent with space group  $P2_1/c$ , which was determined by X-ray diffraction.

	Shimazakiite-4M	Shimazakiite-40	Bond	Shimazakiite-4M	Shimazakiite-40
Ca1-O2	2.340(8)	2.3247(13)	O2-Ca1-O2	98.6(3)	99.39(4)
Ca1-O2	2.340(8)	2.3389(12)	O2-Ca1-O3	80.0(3)	78.07(4)
Ca1-O3	2.356(8)	2.3485(11)	O2-Ca1-O3	78.6(3)	80.57(4)
Ca1-O5	2.373(8)	2.3796(12)	O2-Ca1-O5	82.4(3)	81.82(4)
Ca1-O5	2.394(8)	2.3934(10)	O3-Ca1-O5	89.7(3)	89.20(4)
Ca1-O5	2.417(8)	2.4089(13)	O2-Ca1-O5	77.2(3)	88.88(4)
<ca1-0></ca1-0>	2.370	2.3657	O2-Ca1-O5	88.5(3)	77.17(4)
			O5-Ca1-O5	113.5(2)	113.66(4)
Ca2-O1	2.291(9)	2.3093(11)	O2-Ca1-O5	81.5(3)	80.90(4)
Ca2-O1	2.326(8)	2.3162(11)	O3-Ca1-O5	91.1(3)	91.52(4)
Ca2–O2	2.378(8)	2.3876(11)	O5-Ca1-O5	95.6(3)	95.92(4)
Ca2–O3	2.441(8)	2.4333(12)	O5-Ca1-O5	101.8(2)	101.52(3)
Ca2–O4	2.464(10)	2.4560(12)			~ /
Ca2-O3	2.505(8)	2.5265(13)	O3-B1-O5	125.4(12)	124.26(15)
Ca2-O1	2.626(9)	2.6387(10)	O3-B1-O4	113.3(11)	113.32(15)
<ca2–o></ca2–o>	2.433	2.4382	O5-B1-O4	121.1(11)	122.35(16)
B1-O3	1.329(16)	1.359(2)	O2-B2-O1	121.9(11)	121.42(14)
B1-O5	1.358(16)	1.367(2)	O2-B2-O4	120.7(11)	117.89(13)
B1-O4	1.426(17)	1.430(2)	O1-B2-O4	116.7(11)	120.62(13)
<b1-o></b1-o>	1.371	1.385			
			B1-O4-B2	132.0(11)	131.05(13)
B2-O2	1.320(15)	1.3454(17)			
B2-O1	1.361(16)	1.3627(18)			
B2-O4	1.437(17)	1.4161(19)			
<b2–o></b2–o>	1.373	1.3747			

structures of shimazakiite.

TABLE 5. Interatomic distances (Å) in the crystal TABLE 6. Selected bond angles (°) for the coordination polyhedra in shimazakiite.



FIG. 4. The  $<\bar{1}10>^*-c^*$  electron diffraction pattern of shimazakiite-4*M*. The pattern is streaked along [001]\*. The twin relation between the unit cells is shown by dashed and solid parallelograms.

### Discussion

Shimazakiite, ideally Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub>, has a Ca/B ratio of 1. This is the second highest ratio in the calcium borate minerals after takedaite, Ca<sub>3</sub>B<sub>2</sub>O<sub>6</sub>, which has a Ca/B ratio of 1.5. Two synthetic inorganic phases with the formula Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub> have been described. Hart and Brown (1962) synthesized one of them, and reported powder X-ray diffraction data, but no crystallographic data. Schäfer (1968) reported lattice parameters and powder X-ray diffraction data for the other phase. Ji *et al.* (1993) and Lin *et al.* (1999) independently analysed the crystal structure of Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub>, which has a monoclinic unit cell equivalent to that reported by Schäfer (1968). The powder X-ray diffraction patterns of shimazakiite-4M and shimazakiite-4O differ from those of the two synthetic Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub> phases.

The crystal structures of shimazakiite-4*M* and shimazakiite-4*O* contain  $B_2O_5$  units, produced by corner-sharing between two BO<sub>3</sub> triangles, and 6and 7-coordinate Ca ions. The two BO<sub>3</sub> triangles are almost coplanar and the B–O–B angle of ~130° is reasonable for the *sp*<sup>3</sup> hybrid orbital of the O atom with two lone pairs of electrons in the ordinal borates. The B<sub>2</sub>O<sub>5</sub> units are connected by 6- and 7-coordinate Ca polyhedra to produce a layer structure in the *ab* plane. The layers have



FIG. 5. Illustrations of the crystal structures of shimazakiite-4M (left) and shimazakiite-4O (right) using VESTA (Momma and Izumi, 2011), showing the different stacking sequences of 4 layers of B<sub>2</sub>O<sub>3</sub> and Ca polyhedra.

distinct stacking sequences, which produce the two polytypes shimazakiite-4M and shimazakiite-40 (Fig. 5). The layer is enantiomorphic, shimazakiite-4M contains both right- and lefthanded lavers but shimazakiite-40 contains only one type of layer. Twinning of shimazakiite-4M with a composition plane (001) and twin mirror plane (100) produces the structure of shimazakiite-40 at the twin boundary. This structural relation along with coexistence of these two polytypes explains the abundant polysynthetic twinning in the samples. Two other stacking sequences with the same unit-cell volumes can be produced by the twin law; monoclinic  $P2_1/n$  with unique axis c, and orthorhombic  $P2_1cn$ . These hypothetical structures were not found in the samples that were investigated.

The structural components of shimazakiite, B<sub>2</sub>O<sub>5</sub> units and 6- and 7-coordinate Ca, are the same as those identified in the structures of the synthetic Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub> polymorphs [monoclinic,  $P2_1/c$ , a = 7.234(3), b = 5.181(1), c = 11.524(3) Å,  $\beta =$ 92.94°, V = 431.41 Å<sup>3</sup> (Ji *et al.*, 1993); and monoclinic,  $P2_1/c$ , a = 7.212(2), b = 5.177(1), c =11.498(3) Å,  $\beta = 93.11^{\circ}$ , V = 428.6(4) Å<sup>3</sup> (Lin et al., 1999)]. The configuration of these structural components is different in shimazakiite and the synthetic Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub> structures. In the crystal structures of shimazakiite-4M and shimazakiite-40, the Ca octahedron shares four edges, two with other Ca octahedra and two with 7-coordinate Ca polyhedra; it also shares four corners with four other Ca octahedra. In the crystal structure of synthetic Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub>, the Ca octahedron also shares the four edges, but these are with one other Ca octahedron and three 7-coordinate Ca polyhedra; it shares four corners but these are with two other Ca octahedra and two 7-coordinate Ca polyhedra.

The considerable B deficiency shown by the electron-microprobe analyses and the OH stretching absorption in the IR spectrum indicate partial hydroxylation in shimazakiite. A minor substitution of  $3(OH)^-$  for  $(BO_3)^{3-}$  which may be rewritten  $(B_2O_5)^{3-} \rightarrow [BO_2(OH)]^{2-} + 2(OH)^-$  from a crystal chemical perspective is present.

## Acknowledgements

We would like thank K. Shimada, S. Kishi and M. Tanabe for assistance in the field work. We also wish to thank the Research Instruments Centre of Okayama University of Science for the use of their facilities. The authors would like to express their gratitude to Dr Stuart Mills for his helpful reviews and for correcting the English in the manuscript. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan. Supporting data for single crystal diffraction were measured on an automated 4-circle diffractometer using monochromatic synchrotron radiation at the Beam Line 10A, Photon Factory, High Energy Accelerator Research Organization (PF, KEK), Japan [Project #2012G112].

#### References

- Hart, P.B. and Brown, C.S. (1962) The synthesis of new calcium borate compounds by hydrothermal methods. *Journal of Inorganic and Nuclear Chemistry*, 24, 1057–1065.
- Ji, Y., Liang, J. and Xie, S. (1993) Structure of 2CaO·B<sub>2</sub>O<sub>3</sub>. Acta Crystallographica, C49, 78–79.
- Kusachi, I. and Henmi, C. (1994) Nifontovite and olshanskyite from Fuka, Okayama Prefecture, Japan. *Mineralogical Magazine*, 58, 279–284.
- Kusachi, I., Henmi, C. and Kobayashi, S. (1995) Takedaite, a new mineral from Fuka, Okayama Prefecture, Japan. *Mineralogical Magazine*, 59, 549–552.
- Kusachi, I., Takechi, Y., Henmi, C. and Kobayashi, S. (1998) Parasibirskite, a new mineral from Fuka, Okayama Prefecture, Japan. *Mineralogical Magazine*, 62, 521–525.
- Lin, Q.-S., Cheng, W.-D., Chen, J.-T. and Huang, J.-S. (1999) Calcium pyroborate, Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub>. Acta Crystallographica, C55, 4–6.
- Momma, K. and Izumi, F. (2011) VESTA 3 for threedimensional visualization of crystal, volumetric and morphology data. Journal of Applied Crystallography, 44, 1272-1276.
- Nakamuta, Y. (1999) Precise analysis of a very small mineral by an X-ray diffraction method. *Journal of the Mineralogical Society of Japan*, 28, 117–121, [in Japanese with English abstract].
- Oszlányi, G. and Süto, A. (2004) *Ab initio* structure solution by charge flipping. *Acta Crystallographica*, **A60**, 134–141.
- Oszlányi, G. and Süto, A. (2005) Ab initio structure solution by charge flipping. II. Use of weak reflections. Acta Crystallographica, A61, 147–152.
- Palatinus, L. and Chapuis, G. (2007) Superflip a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. Journal of Applied Crystallography, 40, 786–790.
- Petrova, E.S. (1955) Calciborite, a new mineral. Geology of Mining and Chemical Raw Materials, 218-223, [in Russian].
- Schäfer, U.L. (1968) Synthesis and X-ray diffraction

### SHIMAZAKIITE-4*M* AND SHIMAZAKIITE-4*O*: CA<sub>2</sub>B<sub>2</sub>O<sub>5</sub> POLYTYPES

examination of borates,  $3CaO \cdot B_2O_3$ ,  $2CaO \cdot B_2O_3$  and  $2CaO \cdot B_2O_3 \cdot H_2O$ . *Neues Jahrbuch für Mineralogie, Monatshefte*, **3**, 75–80, [in German with English abstract].

- Sheldrick, G.M. (2008) A short history of *SHELX. Acta Crystallographica*, A64, 112–122.
- Shimazaki, H. (1980) Characteristics of skarn deposits and related acid magmatism in Japan. *Economic Geology*, **75**, 173–183.

Shimazaki, H. and Ozawa, T. (1978) Tsumoite, BiTe, a

new mineral from the Tsumo mine, Japan. *American Mineralogist*, **63**, 1162–1165.

- Toraya, H. (1993) The determination of unit-cell parameters from Bragg reflection data using a standard reference material but without a calibration curve. *Journal of Applied Crystallography*, **26**, 583–590.
- Vasilkova, N.N. (1962) A new calcium borate sibirskite. Zapiski Vsesouznogo Mineralogicheskogo Obshchestva, 91, 455–464, [in Russian].