# Shimazakiite-4M and shimazakiite-4O, $\mathrm{Ca}_{2} \mathrm{~B}_{2} \mathrm{O}_{5}$, two polytypes of a new mineral from Fuka, Okayama Prefecture, Japan 

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## ABSTRACT

Shimazakiite occurs as greyish white aggregates up to 3 mm in diameter. Two polytypes, shimazakiite$4 M$ and shimazakiite- $4 O$, 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 $2 \mathrm{~V}_{\text {calc }}=53^{\circ}$ [shimazakiite- $4 M$ ]; and $\alpha=1.584(2), \beta=1.648(2), \gamma=1.670(2)$ and $2 \mathrm{~V}_{\text {calc }}=54.88^{\circ}$ [shimazakiite-4O]. Quantitative electronmicroprobe analyses (means of 28 and 25 determinations) gave the empirical formulae $\mathrm{Ca}_{2} \mathrm{~B}_{1.92} \mathrm{O}_{4.76}(\mathrm{OH})_{0.24}$ and $\mathrm{Ca}_{2} \mathrm{~B}_{1.92} \mathrm{O}_{4.76}(\mathrm{OH})_{0.24}$ for shimazakiite- $4 M$ and shimazakiite- $4 O$, respectively. The crystal structure refinements: $P 2_{1} / c, a=3.5485(12), b=6.352(2), c=19.254(6) \AA, \beta=$ $92.393(13)^{\circ}, V=433.6(3) \AA^{3}$ [for shimazakiite-4M]; and $P 2_{1} 2_{1} 2_{1}, a=3.55645(8), b=6.35194(15), c=$ 19.2534(5) $\AA, V=434.941(18) \AA^{3}$ [for shimazakiite-4O], converged into $R_{1}$ indices of 0.1273 and 0.0142 , respectively. The crystal structure of shimazakiite consists of a layer containing $\mathrm{B}_{2} \mathrm{O}_{5}$ units (two near-coplanar triangular corner-sharing $\mathrm{BO}_{3}$ 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 $\AA(I)(h k l)]$ are: $3.02(84)(022) ; 2.92(100)(10 \overline{4}) 2.81(56)(104)$; $2.76(32)(113) ; 1.880(32)(11 \overline{8}, 12 \overline{6}, 126,118)$ [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-4O].

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

[^0]mine, Okayama Prefecture, Japan. It has a composition between takedaite, $\mathrm{Ca}_{3} \mathrm{~B}_{2} \mathrm{O}_{6}$ (Kusachi et al., 1995); calciborite, $\mathrm{CaB}_{2} \mathrm{O}_{4}$ (Petrova, 1955); and sibirskite (Vasilkova, 1962) and parasibirskite (Kusachi et al., 1998), both $\mathrm{CaHBO}_{3}$, and is distinct from any previously described synthetic $\mathrm{Ca}_{2} \mathrm{~B}_{2} \mathrm{O}_{5}$ 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 nanometresized 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
$\left(34^{\circ} 46^{\prime} \mathrm{N}, 133^{\circ} 26^{\prime} \mathrm{E}\right)$. 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-4O 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 $\sim 0.9 \times 1.2 \mathrm{~mm}$. Most of the granular crystals without twinning are takedaite or calcite.


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.

Table 1. Chemical composition and analytical data for shimazakiite.

| Constituent | - Shimazakiite-4M - |  | - Shimazakiite-4O - |  | Probe standard |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | (wt.\%) | Range | (wt.\%) | Range |  |
| CaO | 61.09(25) | 60.51-61.46 | 61.30(17) | 60.85-61.50 | Takedaite |
| $\mathrm{B}_{2} \mathrm{O}_{3}$ | 36.39(76) | 34.61-37.76 | 36.51(40) | 35.61-37.35 | Takedaite |
| $\mathrm{H}_{2} \mathrm{O}$ | 2.52* $1.19^{\dagger}$ |  | 2.19* $1.20^{\dagger}$ |  |  |
| Total | 10098.67 |  | $100 \quad 99.01$ |  |  |

[^1]| $\xrightarrow[*]{\text {＊}}$ |  |
| :---: | :---: |
| ＊${ }_{\text {＊}}^{*}$ |  |
| ${ }^{*}$ |  |
| $0^{\circ}$ |  |
| $\xrightarrow[\sim]{\circ}$ |  |
| $\sim$ |  |
| $\because$ | －O－OON－Oー－ーNONNーーmmmomNーm－mmotmNoNm |
| $\approx$ | $0000-00-0-1-1000-10-000-0-100-1 N N-T N 0$ |



 * On the basis of refined lattice parameters from the powder XRD data; $a=3.553(3)$,
$b=6.356(5), c=19.21(5) \AA, \beta=92.16(19)^{\circ}, V=433.4(12) \AA^{3}$.
$* *$ On the basis of refined lattice parameters from the single-crystal XRD data; $a=$
$3.5485(12), b=6.352(2), c=19.254(6) \AA, \beta=92.393(13)^{\circ}, V=433.6(3) \AA^{3}$.
observations were performed using a JEOL JEM2010 transmission electron microscope, operating at an accelerating voltage of 200 kV .

The shimazakiite- $4 M$ 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 $2 \mathrm{~V}_{\text {calc }}=$ $53^{\circ}$ [for shimazakiite-4M]; and $\alpha=1.584(2), \beta=$ 1.648(2), $\gamma=1.670(2)$ and $2 \mathrm{~V}_{\text {calc }}=54.88^{\circ}$ [for shimazakiite-4O]. The mineral is not pleochroic or fluorescent. The mean Vickers microhardness values are $549 \mathrm{~kg} \mathrm{~mm}{ }^{-2}$ (ranging between 516 and $566 \mathrm{~kg} \mathrm{~mm}^{-2}$ ) [for shimazakiite-4M] and $598 \mathrm{~kg} \mathrm{~mm}{ }^{-2}$ (ranging between 480 and $701 \mathrm{~kg} \mathrm{~mm}^{-2}$ ) [for shimazakiite-4O] under a load of 50 g , corresponding to $\sim 41 / 2$ on the Mohs' scale. The density of shimazakiite- $4 O$, measured by immersion in a heavy liquid (Clerici solution) is $2.81(2)$; that of shimazakiite- $4 M$ could not be measured as insufficient pure material was available. The calculated densities are 2.78 and
$2.77 \mathrm{~g} \mathrm{~cm}^{-3}$ 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 $15 \mathrm{kV}, 20 \mathrm{nA}$ with a $5 \mu \mathrm{~m}$ beam diameter. Pure takedaite was used as a standard for Ca and B . The X-ray lines used in the analyses were $\mathrm{B} K \alpha$ (measured using a layered dispersion element) and $\mathrm{CaK} \alpha$ (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 $\pm 0.12 \mathrm{wt} . \%$ for $\mathrm{B}_{2} \mathrm{O}_{3}$ and CaO , respectively. The means of 28 [shimazakiite- $4 M$ ] and 25 [shimaza-kiite-4O] analyses are listed in Table 1. The $\mathrm{H}_{2} \mathrm{O}$ 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 shimaza-kiite- $4 M$ and shimazakiite- $4 O$ are $\mathrm{Ca}_{2} \mathrm{~B}_{1.92}$ $\mathrm{O}_{4.76}(\mathrm{OH})_{0.24}$ and $\mathrm{Ca}_{2} \mathrm{~B}_{1.92} \mathrm{O}_{4.76}(\mathrm{OH})_{0.24}$, respectively. Chemically, shimazakiite varies from compositions which have almost no $\mathrm{H}_{2} \mathrm{O}$ and no B deficiency (e.g. $\mathrm{CaO} 61.29, \mathrm{~B}_{2} \mathrm{O}_{3}$ 37.76;


Fig. 3. The infrared spectrum of shimazakiite-4M.
subtotal 99.05 wt.\% with $\mathrm{Ca}: \mathrm{B}=2: 1.99$ ), to compositions with a B deficiency and corresponding $\mathrm{H}_{2} \mathrm{O}$ (e.g. $\mathrm{CaO} 61.01, \mathrm{~B}_{2} \mathrm{O}_{3}$ 34.61;
subtotal $95.62 \mathrm{wt} . \%$ with $\mathrm{Ca}: \mathrm{B}=2: 1.83$ ). The low analytical total for the B -deficient material suggests substitution of $3(\mathrm{OH})^{-}$for $\left(\mathrm{BO}_{3}\right)^{3-}$.

Table 3. Crystal data, data collection and refinement details for shimazakiite.

|  | Shimazakiite-4M | Shimazakiite-40 |
| :---: | :---: | :---: |
| Crystal dimension (mm) | $0.2 \times 0.1 \times 0.03$ | $0.2 \times 0.1 \times 0.03$ |
| Temperature (K) | 298 | 298 |
| Diffractometer | Rigaku VariMax/R-axis RAPID | Rigaku VariMax/R-axis RAPID |
| Crystal to detector distance (mm) | 127.40 | 127.40 |
| Readout pixel mode (mm) | 0.100 | 0.100 |
| Radiation | MoK $\alpha$ | Mo K $\alpha$ |
| Lattice parameters |  |  |
| $a(\mathrm{~A})$ | 3.5485(12) | 3.55645(8) |
| $b$ ( $\AA$ ) | 6.352(2) | 6.35194(15) |
| $c(\mathrm{~A})$ | 19.254(6) | 19.2534(5) |
| $\beta$ ( ${ }^{\circ}$ ) | 92.393(13) | 90 |
| $V\left(\AA^{3}\right)$ | 433.6(3) | 434.941(18) |
| Extinction rules | $l=2 n$ for $h 0 l$ and $k=2 n$ for $0 k 0$ | $h=2 n$ for $h 00, k=2 n$ for $0 k 0$ and $l=2 n$ for $00 l$ |
| Space group | $P 2{ }_{1} / \mathrm{c}$ | $P 2{ }_{1} 2_{1} 2_{1}$ |
| Z | 4 | 4 |
| Formula | $\mathrm{Ca}_{2}\left(\mathrm{~B}_{2} \mathrm{O}_{5}\right)$ | $\mathrm{Ca}_{2}\left(\mathrm{~B}_{2} \mathrm{O}_{5}\right)$ |
| $D_{\text {calc }}\left(\mathrm{g} \mathrm{cm}^{-3}\right)$ | 2.78 | 2.77 |
| $\mu\left(\mathrm{cm}^{-1}\right)$ | 25.314 | 25.236 |
| $2 \theta$ range ( ${ }^{\circ}$ ) | 6-55 | 6-55 |
| Total oscillation images | 440 | 440 |
| First sweep $\omega$ ( ${ }^{\circ}$ ) | 130.0-190.0 in 0.5 step | 130.0-190.0 in 0.5 step |
| $\chi\left({ }^{\circ}\right)$ | 45.0 | 45.0 |
| $\Phi\left({ }^{\circ}\right)$ | 0.0 | 0.0 |
| exposure rate ( $\mathrm{s}^{\circ}{ }^{\circ}$ ) | 150 | 100 |
| Second sweep $\omega$ ( ${ }^{\circ}$ ) | $0.0-160.0$ in 0.5 step | $0.0-160.0$ in 0.5 step |
| $\chi\left({ }^{\circ}{ }^{\text {a }}\right.$ ) | 45.0 | 45.0 |
| $\varphi\left({ }^{\circ}\right)$ | 180.0 | 180.0 |
| exposure rate ( $\mathrm{s} /{ }^{\circ}$ ) | 150 | 100 |
| Index ranges | $-4 \leqslant h \leqslant 4$ | $-4 \leqslant h \leqslant 4$ |
|  | $-8 \leqslant k \leqslant 8$ | $-7 \leqslant h \leqslant 8$ |
|  | $-24 \leqslant l \leqslant 24$ | $-24 \leqslant h \leqslant 24$ |
| No. measured reflections | 3855 | 4334 |
| No. unique reflections | 1005 | 1005 |
| No. observed reflections [ $1>2 \sigma(I)$ ] | 843 | 995 |
| $R_{\text {int }}$ | 0.0625 | 0.0156 |
| No. of variable parameters | 47 | 83 |
| $R_{1}[1>2 \sigma(I)], \mathrm{R}_{1}$ (all reflections) | $0.1273,0.1379$ | 0.0142, 0.0144 |
| $w R_{2}$ (all reflections) | 0.3632 | 0.0667 |
| Weighting parameters, $\mathrm{a}, \mathrm{b}$ | 0.1, 0 | 0.1, 0 |
| Goodness of fit | 1.446 | 0.674 |
| Final $\Delta \rho_{\text {min }}\left(\mathrm{e} \AA_{\AA^{-3}}{ }^{\text {a }}\right.$ ) | -1.338 | -0.250 |
| Final $\Delta \rho_{\text {max }}\left(\mathrm{e} \AA^{-3}\right)$ | 2.844 | 0.311 |

$R_{1}=\Sigma\left[\left|F_{\mathrm{o}}\right|-\left|F_{\mathrm{c}}\right|\right] / \Sigma\left|F_{\mathrm{o}}\right|$
$w R_{2}=\left\{\Sigma\left[w\left(F_{\mathrm{o}}^{2}-F_{\mathrm{c}}^{2}\right)^{2}\right] / \Sigma\left[w\left(F_{\mathrm{o}}^{2}\right)^{2}\right]\right\}^{1 / 2}$
$w=1 /\left[\sigma^{2}\left(F_{\mathrm{o}}^{2}\right)+(\mathrm{a} P)^{2}+\mathrm{b} P\right]$
$P=\left[2 F_{\mathrm{c}}^{2}+F_{\mathrm{o}}^{2}\right] / 3$
TABLE 4. Fractional atom coordinates and displacement parameters $\left(\AA^{2}\right)$ for shimazakiite

|  | $x / a$ | $y / b$ | $z / c$ | $U_{\text {eq }}$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Shimazakiite-4 $M$ |  |  |  |  |  |  |  |  |  |  |
| 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) |
| Ca 2 | 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) |
| B1 | 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)* |  |  |  |  |  |  |
| O1 | 0.758(2) | 0.8077(13) | 0.0149(4) | 0.0092(18)* |  |  |  |  |  |  |
| O2 | 0.771(2) | 0.8908(12) | 0.1336(4) | $0.0056(16) *$ |  |  |  |  |  |  |
| O3 | 0.285(2) | 0.2684(13) | 0.1481(4) | 0.0068(17)* |  |  |  |  |  |  |
| O4 | 0.972(3) | $0.5495(15)$ | 0.0971(5) | 0.019(2)* |  |  |  |  |  |  |
| O5 | 0.203(2) | 0.5761(13) | 0.2171(4) | 0.0074(17)* |  |  |  |  |  |  |
| Shimazakiite-4O |  |  |  |  |  |  |  |  |  |  |
| Ca 1 | 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) | $0.00014(12)$ | $0.00011(12)$ |
| B1 | 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) |
| O1 | 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) | $0.0011(6)$ |
| O2 | 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) |
| O3 | $0.3157(4)$ | $0.51855(18)$ | 0.14809(6) | 0.0105(3) | 0.0117(6) | 0.0093(5) | 0.0105(5) | 0.0019(4) | 0.0014(5) | 0.0030(6) |
| O4 | 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) |
| O5 | 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) |

[^2]Therefore, although the ideal endmember formula for shimazakiite is $\mathrm{Ca}_{2} \mathrm{~B}_{2} \mathrm{O}_{5}$, the formula taking into account the $3(\mathrm{OH})^{-}$for $\left(\mathrm{BO}_{3}\right)^{3-}$ substitution can be better written $\mathrm{Ca}_{2} \mathrm{~B}_{2-x} \mathrm{O}_{5-3 x}(\mathrm{OH})_{3 x}$, with $x$ $=0-0.2$. The amount of $\mathrm{H}_{2} \mathrm{O}$ 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 $3440 \mathrm{~cm}^{-1}$, and bands in the region $1360-320 \mathrm{~cm}^{-1}$, 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 $1600 \mathrm{~cm}^{-1}$ is likely to be produced by $\mathrm{H}-\mathrm{O}-\mathrm{H}$ 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- $4 M$ and shimazakiite- $4 O$ were obtained using a Gandolfi camera with a diameter of 114.6 mm and Ni -filtered $\mathrm{Cu} K \alpha$ 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- $4 M$ and shima-zakiite- $4 O$ 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 (Oszlányi and Süto, 2004, 2005) using Superflip (Palatinus and Chapuis, 2007). Space group symmetries of $P 2_{1} / c$ and $P 2{ }_{1} 2_{1} 2_{1}$, 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 $\mathrm{Ca}, \mathrm{B}$ 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- $4 M$ and shimazakiite$4 O$, respectively. Owing to the poor quality of the crystal of shimazakiite- $4 M$, 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$4 M$ determined by this analysis is reasonable compared to the crystal structure of shimazakiite$4 O$, which refined to a much more satisfactory $R$ value.

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- $4 M$. 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 $\mathbf{b}^{*}-\mathbf{c}^{*}$ and $\mathbf{c}^{*}-<120>^{*}$ SAED patterns. The electron diffraction patterns show no extinction rules for the $0 k 0$ and $00 l$ reflections, suggesting space groups $P 2, P 2 / m$ or Pm, however as dynamic (multiple) scattering occurs commonly in electron diffraction the SAED patterns are also consistent with space group $P 2_{1} / c$, which was determined by X-ray diffraction.

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Table 5. Interatomic distances ( $\AA$ ) in the crystal structures of shimazakiite.

|  | Shimazakiite-4M | Shimazakiite-4O |
| :--- | :---: | :---: |
| $\mathrm{Ca} 1-\mathrm{O} 2$ | $2.340(8)$ | $2.3247(13)$ |
| $\mathrm{Ca} 1-\mathrm{O} 2$ | $2.340(8)$ | $2.3389(12)$ |
| $\mathrm{Ca} 1-\mathrm{O} 3$ | $2.356(8)$ | $2.3485(11)$ |
| $\mathrm{Ca} 1-\mathrm{O} 5$ | $2.373(8)$ | $2.3796(12)$ |
| $\mathrm{Ca} 1-\mathrm{O} 5$ | $2.394(8)$ | $2.3934(10)$ |
| $\mathrm{Ca} 1-\mathrm{O} 5$ | $2.417(8)$ | $2.4089(13)$ |
| <Ca1-O> | $\mathbf{2 . 3 7 0}$ | $\mathbf{2 . 3 6 5 7}$ |
| $\mathrm{Ca} 2-\mathrm{O} 1$ | $2.291(9)$ | $2.3093(11)$ |
| $\mathrm{Ca} 2-\mathrm{O} 1$ | $2.326(8)$ | $2.3162(11)$ |
| $\mathrm{Ca} 2-\mathrm{O} 2$ | $2.378(8)$ | $2.3876(11)$ |
| $\mathrm{Ca} 2-\mathrm{O} 3$ | $2.441(8)$ | $2.4333(12)$ |
| $\mathrm{Ca} 2-\mathrm{O} 4$ | $2.464(10)$ | $2.4560(12)$ |
| $\mathrm{Ca} 2-\mathrm{O} 3$ | $2.505(8)$ | $2.5265(13)$ |
| $\mathrm{Ca} 2-\mathrm{O} 1$ | $2.626(9)$ | $2.6387(10)$ |
| <Ca2-O> | $\mathbf{2 . 4 3 3}$ | $\mathbf{2 . 4 3 8 2}$ |
|  |  |  |
| $\mathrm{B} 1-\mathrm{O} 3$ | $1.329(16)$ | $1.359(2)$ |
| $\mathrm{B} 1-\mathrm{O} 5$ | $1.358(16)$ | $1.367(2)$ |
| $\mathrm{B} 1-\mathrm{O} 4$ | $1.426(17)$ | $1.430(2)$ |
| <B1-O> | $\mathbf{1 . 3 7 1}$ | $\mathbf{1 . 3 8 5}$ |
| B2-O2 | $1.320(15)$ | $1.3454(17)$ |
| $\mathrm{B} 2-\mathrm{O} 1$ | $1.361(16)$ | $1.3627(18)$ |
| $\mathrm{B} 2-\mathrm{O} 4$ | $1.437(17)$ | $1.4161(19)$ |
| <B2-O> | $\mathbf{1 . 3 7 3}$ | $\mathbf{1 . 3 7 4 7}$ |
|  |  |  |

Table 6. Selected bond angles $\left({ }^{\circ}\right)$ for the coordination polyhedra in shimazakiite.

| Bond | Shimazakiite-4M | Shimazakiite-4O |
| :--- | :---: | :---: |
| O2-Ca1-O2 | $98.6(3)$ | $99.39(4)$ |
| O2-Ca1-O3 | $80.0(3)$ | $78.07(4)$ |
| O2-Ca1-O3 | $78.6(3)$ | $80.57(4)$ |
| O2-Ca1-O5 | $82.4(3)$ | $81.82(4)$ |
| O3-Ca1-O5 | $89.7(3)$ | $89.20(4)$ |
| O2-Ca1-O5 | $77.2(3)$ | $88.88(4)$ |
| O2-Ca1-O5 | $88.5(3)$ | $77.17(4)$ |
| O5-Ca1-O5 | $113.5(2)$ | $113.66(4)$ |
| O2-Ca1-O5 | $81.5(3)$ | $80.90(4)$ |
| O3-Ca1-O5 | $91.1(3)$ | $91.52(4)$ |
| O5-Ca1-O5 | $95.6(3)$ | $95.92(4)$ |
| O5-Ca1-O5 | $101.8(2)$ | $101.52(3)$ |
| O3-B1-O5 | $125.4(12)$ | $124.26(15)$ |
| O3-B1-O4 | $113.3(11)$ | $113.32(15)$ |
| O5-B1-O4 | $121.1(11)$ | $122.35(16)$ |
| O2-B2-O1 | $121.9(11)$ | $121.42(14)$ |
| O2-B2-O4 | $120.7(11)$ | $117.89(13)$ |
| O1-B2-O4 | $116.7(11)$ | $120.62(13)$ |
| B1-O4-B2 | $132.0(11)$ | $131.05(13)$ |



Fig. 4. The $<\overline{1} 10>^{*}-\mathbf{c}^{*}$ 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 $\mathrm{Ca}_{2} \mathrm{~B}_{2} \mathrm{O}_{5}$, has a $\mathrm{Ca} / \mathrm{B}$ ratio of 1. This is the second highest ratio in the calcium borate minerals after takedaite, $\mathrm{Ca}_{3} \mathrm{~B}_{2} \mathrm{O}_{6}$, which has a $\mathrm{Ca} / \mathrm{B}$ ratio of 1.5 . Two synthetic inorganic phases with the formula $\mathrm{Ca}_{2} \mathrm{~B}_{2} \mathrm{O}_{5}$ 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 $\mathrm{Ca}_{2} \mathrm{~B}_{2} \mathrm{O}_{5}$, which has a monoclinic
unit cell equivalent to that reported by Schäfer (1968). The powder X-ray diffraction patterns of shimazakiite- $4 M$ and shimazakiite- $4 O$ differ from those of the two synthetic $\mathrm{Ca}_{2} \mathrm{~B}_{2} \mathrm{O}_{5}$ phases.

The crystal structures of shimazakiite- $4 M$ and shimazakiite $-4 O$ contain $\mathrm{B}_{2} \mathrm{O}_{5}$ units, produced by corner-sharing between two $\mathrm{BO}_{3}$ triangles, and 6and 7-coordinate Ca ions. The two $\mathrm{BO}_{3}$ triangles are almost coplanar and the $\mathrm{B}-\mathrm{O}-\mathrm{B}$ angle of $\sim 130^{\circ}$ is reasonable for the $s p^{3}$ hybrid orbital of the O atom with two lone pairs of electrons in the ordinal borates. The $\mathrm{B}_{2} \mathrm{O}_{5}$ units are connected by 6- and 7-coordinate Ca polyhedra to produce a layer structure in the $a b$ plane. The layers have


Fig. 5. Illustrations of the crystal structures of shimazakiite- $4 M$ (left) and shimazakiite- $4 O$ (right) using VESTA (Momma and Izumi, 2011), showing the different stacking sequences of 4 layers of $\mathrm{B}_{2} \mathrm{O}_{3}$ and Ca polyhedra.
distinct stacking sequences, which produce the two polytypes shimazakiite- $4 M$ and shimazakiite$4 O$ (Fig. 5). The layer is enantiomorphic, shimazakiite- $4 M$ contains both right- and lefthanded layers but shimazakiite- $4 O$ contains only one type of layer. Twinning of shimazakiite- $4 M$ with a composition plane (001) and twin mirror plane (100) produces the structure of shimaza-kiite- $4 O$ 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 $P 2_{1} / n$ with unique axis $c$, and orthorhombic $P 2_{1} c n$. These hypothetical structures were not found in the samples that were investigated.
The structural components of shimazakiite, $\mathrm{B}_{2} \mathrm{O}_{5}$ units and 6- and 7-coordinate Ca , are the same as those identified in the structures of the synthetic $\mathrm{Ca}_{2} \mathrm{~B}_{2} \mathrm{O}_{5}$ polymorphs [monoclinic, $P 2_{1} / c$, $a=7.234(3), b=5.181(1), c=11.524(3) \AA, \beta=$ $92.94^{\circ}, V=431.41 \AA^{3}$ (Ji et al., 1993); and monoclinic, $P 2_{1} / c, a=7.212(2), b=5.177(1), c=$ 11.498(3) $\AA, \beta=93.11^{\circ}, V=428.6$ (4) $\AA^{3}$ (Lin et al., 1999)]. The configuration of these structural components is different in shimazakiite and the synthetic $\mathrm{Ca}_{2} \mathrm{~B}_{2} \mathrm{O}_{5}$ structures. In the crystal structures of shimazakiite- $4 M$ and shimazakiite$4 O$, 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 $\mathrm{Ca}_{2} \mathrm{~B}_{2} \mathrm{O}_{5}$, 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 $3(\mathrm{OH})^{-}$for $\left(\mathrm{BO}_{3}\right)^{3-}$ which may be rewritten $\left(\mathrm{B}_{2} \mathrm{O}_{5}\right)^{3-} \rightarrow\left[\mathrm{BO}_{2}(\mathrm{OH})\right]^{2-}+2(\mathrm{OH})^{-}$ from a crystal chemical perspective is present.

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[^1]:    * Water content by difference.
    ${ }^{\dagger}$ Water content re-calculated based on the stoichiometry $\mathrm{Ca}_{2} \mathrm{~B}_{2-x} \mathrm{O}_{5-3 x}(\mathrm{OH})_{3 x}$.

[^2]:    * These are $U_{\text {iso }}$.

