

# Redetermination of ruizite, $\text{Ca}_2\text{Mn}^{3+}_2[\text{Si}_4\text{O}_{11}(\text{OH})_2](\text{OH})_2 \cdot 2\text{H}_2\text{O}$

Kim V. Fendrich,\* Robert T. Downs and Marcus J. Origlieri

University of Arizona, 1040 E. 4th Street, Tucson, AZ 85721, USA. \*Correspondence e-mail: kfendrich@email.arizona.edu

Received 29 April 2016

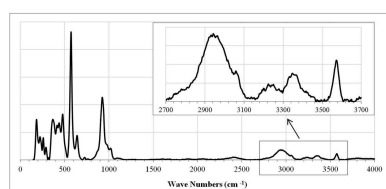
Accepted 6 June 2016

Edited by M. Weil, Vienna University of  
Technology, Austria**Keywords:** crystal structure; redetermination;  
ruizite; finite silicate chain.**CCDC reference:** 1483820**Supporting information:** this article has  
supporting information at journals.iucr.org/e

The crystal structure of ruizite, ideally  $\text{Ca}_2\text{Mn}^{3+}_2[\text{Si}_4\text{O}_{11}(\text{OH})_2](\text{OH})_2 \cdot 2\text{H}_2\text{O}$  [dicalcium dimanganese(III) tetrasilicate tetrahydroxide dihydrate] was first determined in space group  $A2$  with an isotropic displacement parameter model ( $R = 5.6\%$ ) [Hawthorne (1984). *Tschermaks Mineral. Petrogr. Mitt.* **33**, 135–146]. A subsequent refinement in space group  $C2/m$  with anisotropic displacement parameters for non-H atoms converged with  $R = 8.4\%$  [Moore *et al.* (1985). *Am. Mineral.* **70**, 171–181]. The current study reports a redetermination of the ruizite structure by means of single-crystal X-ray diffraction data of a natural sample from the Wessels mine, Kalahari Manganese Field, Northern Cape Province, South Africa. Our data ( $R_1 = 3.0\%$ ) confirm that the space group of ruizite is that of the first study rather than  $C2/m$ . This work improves upon the structure reported by Hawthorne (1984) in that all non-H atoms were refined with anisotropic displacement parameters and all hydrogen atoms were located. The crystal structure consists of [010] chains of edge-sharing  $\text{MnO}_6$  octahedra flanked by finite  $[\text{Si}_4\text{O}_{11}(\text{OH})_2]$  chains. The  $\text{Ca}^{2+}$  cations are situated in the cavities of this arrangement and exhibit a coordination number of seven.

## 1. Mineralogical and crystal-chemical context

Ruizite from the Christmas mine, Gila County, Arizona, USA, was originally described by Williams & Duggan (1977) with monoclinic symmetry in the space group  $P2_1/c$  and unit-cell parameters  $a = 11.95$ ,  $b = 6.17$ ,  $c = 9.03$  Å,  $\beta = 91.38^\circ$  based on rotation and Weissenberg photographs. Ideal chemistry was



**Figure 1**  
Photograph of the ruizite specimen analyzed in this study.

**Table 1**  
Chemical composition and unit-cell parameters (Å, Å<sup>3</sup>) of different ruizite samples.

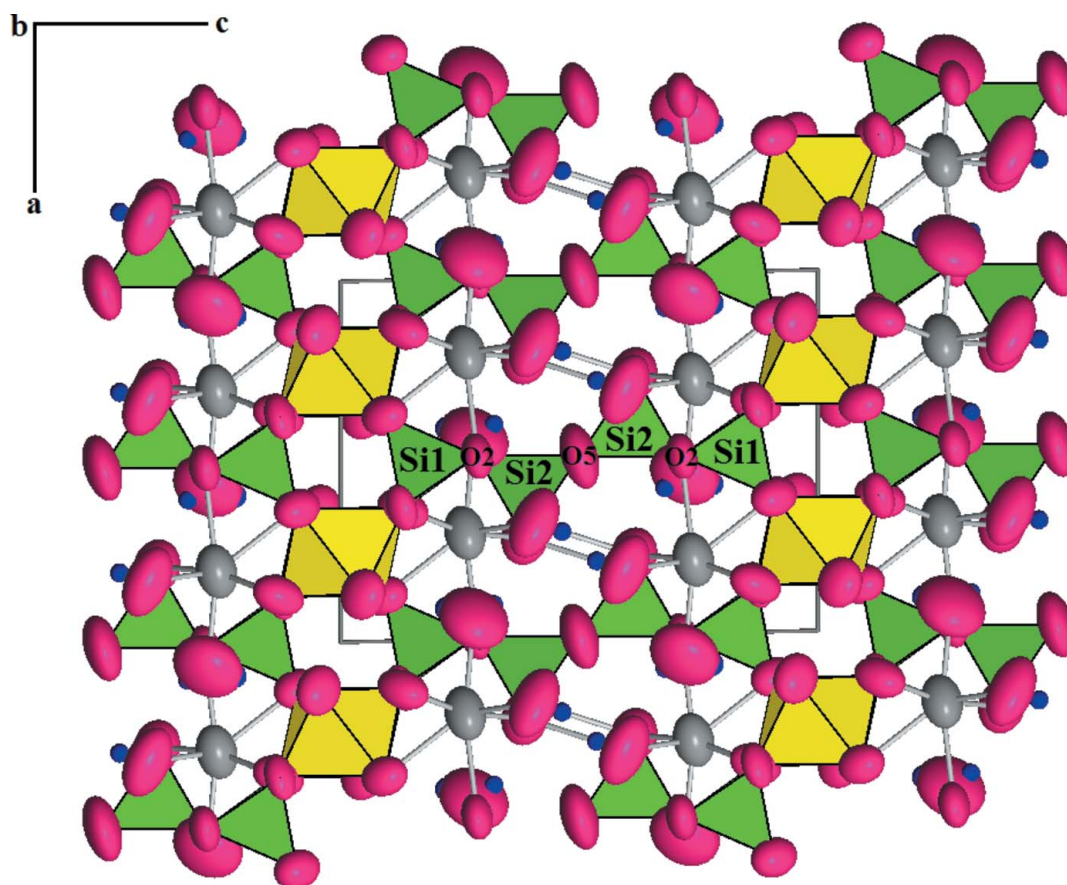
Chemistry	<i>a</i>	<i>b</i>	<i>c</i>	$\beta$	<i>V</i>	Space group	Reference and locality
(Ca <sub>1.90</sub> Sr <sub>0.06</sub> Mg <sub>0.04</sub> )(Mn <sup>3+</sup> <sub>1.88</sub> Fe <sup>3+</sup> <sub>0.07</sub> Al <sub>0.05</sub> )-Si <sub>4.01</sub> O <sub>11</sub> (OH) <sub>4</sub> ·2H <sub>2</sub> O	9.0360 (3)	6.1683 (2)	11.9601 (4)	91.433 (2)	666.41 (4)	C2	Present study R130787, Wessels mine
(Ca <sub>1.96</sub> Mg <sub>0.02</sub> ) <sub>Σ=1.98</sub> (Mn <sup>3+</sup> <sub>1.97</sub> Fe <sup>3+</sup> <sub>0.04</sub> Al <sub>0.01</sub> ) <sub>Σ=2.02</sub> -Si <sub>4.01</sub> O <sub>11</sub> (OH) <sub>4</sub> ·2H <sub>2</sub> O	9.0476 (6)	6.1774 (3)	11.9707 (8)	91.344 (3)	668.9 (1)	C2	R140132, Cornwall mine
(Ca <sub>1.98</sub> Mg <sub>0.03</sub> ) <sub>Σ=2.01</sub> (Mn <sup>3+</sup> <sub>1.95</sub> Fe <sup>3+</sup> <sub>0.08</sub> V <sup>3+</sup> <sub>0.01</sub> ) <sub>Σ=2.04</sub> -Si <sub>3.96</sub> O <sub>11</sub> (OH) <sub>4</sub> ·2H <sub>2</sub> O	9.056 (5)	6.170 (3)	11.92 (1)	91.30 (4)	666.1 (3)		R060930, Christmas mine
Ca <sub>2</sub> Mn <sup>3+</sup> <sub>2</sub> (OH) <sub>2</sub> [Si <sub>4</sub> O <sub>11</sub> (OH) <sub>2</sub> ]·2H <sub>2</sub> O	9.064 (1)	6.171 (2)	11.976 (3)	91.38 (2)	669.7 (4)	C2/m	Moore <i>et al.</i> (1985), N'Chwaning mine
Ca <sub>2</sub> Mn <sup>3+</sup> <sub>2</sub> [Si <sub>4</sub> O <sub>11</sub> (OH) <sub>2</sub> ](OH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	11.974 (3)	6.175 (2)	9.052 (2)	91.34 (2)	669.1 (4)	A2	Hawthorne (1984), Wessels mine
Ca <sub>1.89</sub> Mn <sup>3+</sup> <sub>2.13</sub> [Si <sub>3.96</sub> O <sub>11</sub> (OH) <sub>2</sub> ](OH) <sub>2</sub> ·2H <sub>2</sub> O*							Wilson & Dunn (1978), Wessels mine
Ca <sub>1.06</sub> Mn <sup>3+</sup> <sub>0.86</sub> (SiO <sub>3</sub> ) <sub>1.89</sub> (OH) <sub>1.03</sub> ·2.06H <sub>2</sub> O	11.95	6.17	9.03	91.38	665.6	P2 <sub>1</sub> /c	Williams & Duggan (1977), Christmas mine

\* Recalculated based on 17 O atoms, as in the currently accepted formula.

proposed as CaMn(SiO<sub>3</sub>)<sub>2</sub>(OH)·2H<sub>2</sub>O. Wilson & Dunn (1978) reported a second occurrence of ruizite from the Wessels mine, Kalahari Manganese Field, Northern Cape Province, South Africa, with the same chemical formula as that given by Williams & Duggan (1977).

To date, ruizite has been found at five different localities (Table 1): Christmas mine, Gila County, Arizona, USA (Williams & Duggan, 1977); Wessels mine (Wilson & Dunn,

1978) and N'Chwaning mines (Moore *et al.*, 1985) in the Northern Cape Province, South Africa; Cornwall mine, Lebanon County, Pennsylvania, USA (Kearns & Kearns, 2008); and the Cerchiara mine, Liguria, Italy (Balestra *et al.*, 2009). It is a product of retrograde metamorphism and oxidation during cooling of calc-silicate rocks formed *via* contact metamorphism of limestones (Williams & Duggan, 1977). The secondary mineralization of ruizite at the type



**Figure 2**  
The crystal structure of ruizite as reported in this paper, viewed down *b*. Pink and gray ellipsoids represent O and Ca atoms, respectively. SiO<sub>4</sub> tetrahedra are shown in green and MnO<sub>6</sub> octahedra in yellow. Hydrogen atoms are represented by small dark-blue spheres.

**Table 2**  
Hydrogen-bond geometry (Å, °).

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
O7—H1···O6 <sup>i</sup>	0.73 (6)	1.94 (6)	2.662 (4)	168 (8)
O8—H2···O9	0.64 (6)	2.28 (6)	2.842 (4)	149 (9)
O9—H3···O6	0.74 (8)	2.06 (8)	2.737 (6)	153 (7)
O9—H4···O8	0.72 (6)	2.14 (6)	2.842 (4)	167 (9)

Symmetry code: (i)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + 1$ .

locality may have occurred during the Cretaceous or sometime thereafter (Peterson & Swanson, 1956).

The structure of ruizite was first determined by Hawthorne (1984) on the basis of space group *A2*, in the same setting as reported by Williams & Duggan (1977), using a crystal from the Wessels mine. The structure refinement yielded an *R* factor of 5.6% for an isotropic displacement model in which positions of three of the four hydrogen atoms were located. Refinement of anisotropic displacement parameters was not successful. The ideal chemical formula was revised to  $\text{Ca}_2\text{Mn}^{\text{III}}_2[\text{Si}_4\text{O}_{11}(\text{OH})_2](\text{OH})_2(\text{H}_2\text{O})_2$ . Moore *et al.* (1985) re-examined the ruizite structure using a sample from the N'Chwaning mine and reported space group *C2/m*, a cell setting different from that adopted by Hawthorne (1984). The structure was refined with anisotropic displacement parameters for non-H atoms, yielding an *R* factor of 8.4%; no hydrogen atoms were located. However, most of the resulting displacement ellipsoids were unreasonable or non-positive definite. Moore *et al.* (1985) presented a disclaimer that ‘the anisotropic thermal parameters for these crystals are more likely manifestations of intergrowths and domain disorder, rather than descriptions of true thermal motions’.

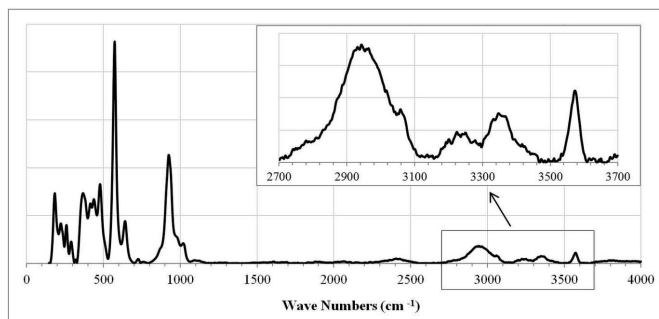
The current study reports a redetermination of the ruizite structure by means of single-crystal X-ray diffraction data of a natural sample from the Wessels mine, Kalahari Manganese Field, Northern Cape Province, South Africa (Fig. 1).

## 2. Structural commentary

The structure of ruizite is characterized by chains of edge-sharing  $\text{MnO}_6$  octahedra extending along [010], which are linked by corner-sharing with  $\text{SiO}_4$  tetrahedra that form short  $[\text{Si}_4\text{O}_{11}(\text{OH})_2]$  chains, giving rise to a three-dimensional network (Fig. 2). The finite  $[\text{Si}_4\text{O}_{11}(\text{OH})_2]$  chain in ruizite is the only reported silicate chain of this type. The relatively large  $\text{Ca}^{2+}$  cations occupy the interstitial cavities and exhibit a coordination number of seven [Ca—O bond-length range

**Table 3**  
Bond-valence sums.

	O1	O2	O3	O4	O5	O6	O7	O8	O9	$\Sigma_{\text{M}}$
Ca	0.203	0.178	0.292	0.284		0.357	0.272		0.322	<b>2.014</b>
Mn	0.317 <sub>x24</sub> →		0.674	0.668				0.599 <sub>x2</sub> →		<b>3.173</b>
Si1	1.044	0.898	0.971	1.036						<b>3.949</b>
Si2		0.957			1.058 <sub>x24</sub>	1.087	0.953			<b>4.055</b>
$\Sigma_{\text{O}}$	<b>1.881</b>	<b>2.033</b>	<b>1.937</b>	<b>1.988</b>	<b>2.116</b>	<b>1.444</b>	<b>1.225</b>	<b>1.198</b>	<b>0.322</b>	



**Figure 3**  
Broad-scan Raman spectrum of an unoriented ruizite specimen (R130787).

2.348 (4)–2.606 (3) Å]. The  $\text{Mn}^{3+}$  cations are bonded to four O atoms (O3, O4, and two O1 atoms) and two OH groups (O8—H2), resulting in a distorted  $\text{MnO}_6$  octahedron, with an octahedral angle variance of 27.35 and a quadratic elongation index of 1.015 (Robinson *et al.*, 1971). The  $\text{Si1O}_4$  tetrahedron is more distorted than  $\text{Si2O}_4$ , as indicated by angular variances (26.37 vs 10.18) and quadratic elongation indices (1.007 vs 1.003). Both average Si1— $\text{O}_{\text{nbr}}$  and Si2— $\text{O}_{\text{nbr}}$  bond lengths (nbr = non-bridging) are 1.618 Å. The Si2—O7 separation (1.642 Å) is longer than the average Si2— $\text{O}_{\text{nbr}}$  length because O7 is the hydroxyl group that is also bonded to a  $\text{Ca}^{2+}$  cation. The O5 atom is located on a twofold rotation axis and bridges the two Si2 atoms with a Si—O bond length of 1.6031 (13) Å, which is most likely a result of the considerably large Si2—O5—Si2 angle [162.9 (3)°] when compared to the Si1—O2—Si2 angle [128.27 (18)°] (Gibbs *et al.*, 1994).

The hydrogen-bonding scheme in ruizite is presented in Table 2. The O9 atom is bonded to atoms H3 and H4, forming a water molecule whereas the O7 and O8 atoms are bonded to H1 and H2, respectively, to form two distinct OH groups. The bond-valence calculations (Brown, 2002) confirm the model (Table 3). The O6 atom is markedly underbonded because it is an acceptor for both H1 and H3, and consequently it is associated with the shortest Si—O and Ca—O bond lengths. It is interesting to note that all hydrogen bonds in ruizite are shorter than 2.85 Å (Table 2). Nevertheless, the Raman spectrum shows a relatively sharp band at 3570  $\text{cm}^{-1}$  (see below). According to Libowitzky (1999), this band would correspond to a hydrogen bond length (O···O) of 3.1–3.3 Å. Perhaps O7—H1 forms a bifurcated hydrogen bond, where H1 is bonded to both O6 and O5. The O7···O5 distance is 3.354 Å, which could explain the band at 3570  $\text{cm}^{-1}$  (Libowitzky, 1999).

**Table 4**  
Experimental details.

Crystal data	
Chemical formula	$\text{Ca}_2\text{Mn}^{3+}_2[\text{Si}_4\text{O}_{11}(\text{OH})_2](\text{OH})_2 \cdot 2\text{H}_2\text{O}$
$M_r$	582.46
Crystal system, space group	Monoclinic, $C2$
Temperature (K)	293
$a, b, c$ (Å)	9.0360 (3), 6.1683 (2), 11.9601 (4)
$\beta$ (°)	91.433 (2)
$V$ (Å <sup>3</sup> )	666.41 (4)
$Z$	2
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	3.13
Crystal size (mm)	0.06 × 0.04 × 0.04
Data collection	
Diffraction	Bruker APEXII CCD area-detector
Absorption correction	Multi-scan (SADABS; Bruker, 2004)
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	4997, 2038, 1732
$R_{\text{int}}$	0.029
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.758
Refinement	
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.030, 0.065, 1.06
No. of reflections	2038
No. of parameters	127
No. of restraints	1
H-atom treatment	Only H-atom coordinates refined
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.60, -0.53
Absolute structure	Refined as an inversion twin.
Absolute structure parameter	0.18 (5)

Computer programs: APEX2 and SAINT (Bruker, 2004), SHELXT (Sheldrick, 2015a), SHELXL2014/7 (Sheldrick, 2015b), XtalDraw (Downs & Hall-Wallace, 2003) and publCIF (Westrip, 2010).

Fig. 3 is a plot of the Raman spectrum of ruizite. A tentative assignment of the major Raman bands is as follows: The bands between 2800 and 3600 cm<sup>-1</sup> are due to the O—H stretching vibrations. The short H2···H4 distance (1.58 Å) may be a result of disordering of one of the hydrogen atoms, which may also explain the considerably broad O—H stretching band in the Raman spectrum around 2940 cm<sup>-1</sup>. The bands in the 1050–800 cm<sup>-1</sup> region can be attributed to the Si—O stretching vibrations within the SiO<sub>4</sub> groups and those in the range of 670–520 cm<sup>-1</sup> to the O—Si—O bending vibrations within the SiO<sub>4</sub> tetrahedra. The bands below 500 cm<sup>-1</sup> are mainly associated with the rotational and translational modes of SiO<sub>4</sub> tetrahedra, and the MnO<sub>6</sub> and CaO<sub>7</sub> polyhedral interactions.

### 3. Synthesis and crystallization

The ruizite crystal used in this study is from the Wessels mine, Kalahari Manganese Field, Northern Cape Province, South Africa (Fig. 1) and is in the collection of the RRUFF project (<http://rruff.info/R130787>). Its chemical composition was measured using a CAMECA SX 100 electron microprobe at the conditions of 15 keV, 20 nA and a beam size <1 µm. The composition, calculated on the basis of 17 oxygen atoms and

an estimation of H<sub>2</sub>O by difference is (Ca<sub>1.90</sub>Sr<sub>0.06</sub>Mg<sub>0.04</sub>)-(Mn<sup>3+</sup><sub>1.88</sub>Fe<sup>3+</sup><sub>0.07</sub>Al<sub>0.05</sub>)Si<sub>4.01</sub>O<sub>11</sub>(OH)<sub>4</sub>·2H<sub>2</sub>O.

The Raman spectrum of ruizite was collected from a randomly oriented crystal at 100% power of 150 mW on a Thermo Almega microRaman system, using a solid-state laser with a wavelength of 532 nm, and a thermoelectrically cooled CCD detector. The laser was partially polarized with 4 cm<sup>-1</sup> resolution and a spot size of 1 µm.

### 4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The crystal structure was solved and refined based on space group  $C2$  because it yielded better refinement statistics than in  $C2/m$  in terms of bond lengths and angles, atomic displacement parameters, and  $R$  factors. The crystal under investigation was twinned by inversion (Table 4). Electron microprobe analysis revealed that the ruizite sample studied contains small amounts of Sr, Mg, Fe, and Al. However, the overall effects of minor and trace amounts of these elements are negligible; therefore, the ideal chemical formula  $\text{Ca}_2\text{Mn}^{3+}_2[\text{Si}_4\text{O}_{11}(\text{OH})_2](\text{OH})_2 \cdot 2\text{H}_2\text{O}$  was assumed during refinement. The H atoms were located from difference Fourier syntheses and confirmed by bond valence sum calculations. Their positions were refined with a fixed isotropic displacement parameter ( $U_{\text{iso}} = 0.04$ ). The maximum residual electron density in the difference Fourier map, 0.60 e Å<sup>-3</sup>, was located at 0.85 Å from O8 and the minimum density at 0.17 Å from H4.

### Acknowledgements

The authors gratefully acknowledge support of this study from the Arizona Science Foundation and NASA NNX11AP82A, Mars Science Laboratory Investigations. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Aeronautics and Space Administration.

### References

- Balestra, C., Kolitsch, U., Blass, G., Callegari, A. M., Boiocchi, M., Armellino, G., Ciriotti, M. E., Ambrino, P. & Bracco, R. (2009). *Micro*, **1**–2009, 78–99.
- Brown, I. D. (2002). *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*. Oxford University Press.
- Bruker (2004). SADABS, APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Downs, R. T. & Hall-Wallace, M. (2003). *Am. Mineral.* **88**, 247–250.
- Gibbs, G. V., Downs, J. W. & Boisen, M. B. (1994). *Rev. Min. Geochem.* **29**, 332–368.
- Hawthorne, F. C. (1984). *Tschermaks Mineral. Petrogr. Mitt.* **33**, 135–146.
- Kearns, L. E. & Kearns, C. A. (2008). *Mineral. News*, **24**, 8–9.
- Libowitzky, E. (1999). *Monatsh. Chem.* **130**, 1047–1059.
- Moore, P. B., Shen, J. & Araki, T. (1985). *Am. Mineral.* **70**, 171–181.
- Peterson, N. P. & Swanson, R. W. (1956). *U. S. Geol. Surv. Bull.* **1027–H**, 351–373.
- Robinson, K., Gibbs, G. V. & Ribbe, P. H. (1971). *Science*, **172**, 567–570.

Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.  
Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.  
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Williams, S. A. & Duggan, M. (1977). *Mineral. Mag.* **41**, 429–432.  
Wilson, W. E. & Dunn, P. J. (1978). *Miner. Rec.* **9**, 137–153.



## supporting information

*Acta Cryst.* (2016). E72, 959-963 [https://doi.org/10.1107/S2056989016009129]

Redetermination of ruizite,  $\text{Ca}_2\text{Mn}^{3+}_2[\text{Si}_4\text{O}_{11}(\text{OH})_2](\text{OH})_2 \cdot 2\text{H}_2\text{O}$ 

Kim V. Fendrich, Robert T. Downs and Marcus J. Origlieri

## Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINTE* (Bruker, 2004); data reduction: *SAINTE* (Bruker, 2004); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015b); molecular graphics: *XtalDraw* (Downs & Hall-Wallace, 2003); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

## Dicalcium dimanganese(III) tetrasilicate tetrahydroxide dihydrate

## Crystal data

$\text{Ca}_2\text{H}_8\text{Mn}_2\text{O}_{17}\text{Si}_4$   
 $M_r = 582.46$   
 Monoclinic, *C2*  
 $a = 9.0360$  (3) Å  
 $b = 6.1683$  (2) Å  
 $c = 11.9601$  (4) Å  
 $\beta = 91.433$  (2)°  
 $V = 666.41$  (4) Å<sup>3</sup>  
 $Z = 2$

$F(000) = 580$   
 $D_x = 2.903$  Mg m<sup>-3</sup>  
 Mo *K*α radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 1284 reflections  
 $\theta = 8.0\text{--}63.1^\circ$   
 $\mu = 3.13$  mm<sup>-1</sup>  
 $T = 293$  K  
 Prismatic, brown  
 $0.06 \times 0.04 \times 0.04$  mm

## Data collection

Bruker APEXII CCD area-detector  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 $\varphi$  and  $\omega$  scan  
 Absorption correction: multi-scan  
 (*SADABS*; Bruker, 2004)

2038 independent reflections  
 1732 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.029$   
 $\theta_{\text{max}} = 32.6^\circ$ ,  $\theta_{\text{min}} = 4.0^\circ$   
 $h = -13 \rightarrow 13$   
 $k = -9 \rightarrow 8$   
 $l = -18 \rightarrow 18$

4997 measured reflections

## Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.030$   
 $wR(F^2) = 0.065$   
 $S = 1.06$   
 2038 reflections  
 127 parameters  
 1 restraint  
 Hydrogen site location: difference Fourier map

Only H-atom coordinates refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0243P)^2 + 0.6718P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.60$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.53$  e Å<sup>-3</sup>  
 Absolute structure: Refined as an inversion  
 twin.  
 Absolute structure parameter: 0.18 (5)

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refined as a 2-component inversion twin.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ca	0.29482 (8)	0.9839 (2)	0.73974 (6)	0.01019 (15)
Mn	0.74915 (13)	0.7373 (2)	0.99906 (10)	0.00679 (12)
Si1	0.96440 (10)	0.9873 (3)	0.84877 (8)	0.00607 (18)
Si2	0.89549 (12)	1.0016 (3)	0.60450 (9)	0.0084 (2)
O1	0.1260 (3)	0.9855 (9)	0.9082 (2)	0.0088 (5)
O2	1.0076 (3)	0.9891 (10)	0.71434 (19)	0.0094 (5)
O3	0.8652 (5)	0.7699 (7)	0.8692 (4)	0.0096 (9)
O4	0.1302 (4)	0.2031 (7)	0.1276 (3)	0.0070 (9)
O5	1.0000	1.0402 (7)	0.5000	0.0169 (11)
O6	0.7769 (4)	1.1913 (6)	0.6146 (3)	0.0121 (8)
O7	0.8183 (4)	0.7611 (6)	0.5947 (3)	0.0152 (9)
O8	0.6317 (3)	0.9886 (9)	0.9535 (2)	0.0096 (5)
O9	0.5570 (4)	0.9743 (11)	0.7213 (3)	0.0201 (8)
H1	0.792 (8)	0.760 (12)	0.536 (6)	0.040*
H2	0.617 (7)	1.029 (13)	0.905 (5)	0.040*
H3	0.594 (7)	1.041 (13)	0.679 (6)	0.040*
H4	0.586 (6)	0.967 (18)	0.778 (5)	0.040*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ca	0.0129 (4)	0.0101 (3)	0.0076 (3)	−0.0017 (6)	0.0017 (3)	−0.0006 (6)
Mn	0.0074 (2)	0.0068 (2)	0.0062 (2)	0.00026 (19)	0.00176 (17)	0.00027 (18)
Si1	0.0063 (4)	0.0071 (4)	0.0049 (4)	−0.0002 (8)	0.0009 (3)	0.0002 (8)
Si2	0.0101 (5)	0.0100 (6)	0.0051 (4)	−0.0020 (7)	0.0008 (4)	−0.0003 (7)
O1	0.0071 (11)	0.0098 (10)	0.0094 (12)	0.001 (2)	−0.0006 (9)	−0.002 (2)
O2	0.0094 (12)	0.0142 (11)	0.0045 (11)	−0.001 (2)	0.0012 (9)	0.000 (2)
O3	0.007 (2)	0.010 (2)	0.012 (2)	−0.0012 (16)	0.0025 (18)	−0.0024 (17)
O4	0.009 (2)	0.007 (2)	0.005 (2)	−0.0014 (16)	0.0018 (17)	0.0005 (15)
O5	0.019 (2)	0.025 (3)	0.007 (2)	0.000	0.0043 (17)	0.000
O6	0.0127 (18)	0.0138 (17)	0.0096 (17)	0.0018 (14)	−0.0006 (14)	−0.0011 (13)
O7	0.021 (2)	0.0131 (17)	0.0112 (19)	−0.0035 (16)	−0.0054 (16)	0.0001 (15)
O8	0.0113 (12)	0.0087 (10)	0.0088 (12)	0.001 (2)	−0.0006 (10)	−0.003 (2)
O9	0.0172 (16)	0.0221 (19)	0.0213 (17)	−0.006 (2)	0.0042 (13)	0.001 (3)

Geometric parameters (Å, °)

Ca—O6 <sup>i</sup>	2.348 (4)	Mn—O1 <sup>vii</sup>	2.184 (4)
Ca—O9	2.386 (4)	Mn—O1 <sup>viii</sup>	2.187 (4)
Ca—O3 <sup>ii</sup>	2.422 (5)	Si1—O1 <sup>ix</sup>	1.608 (3)
Ca—O4 <sup>iii</sup>	2.433 (4)	Si1—O4 <sup>x</sup>	1.611 (4)
Ca—O7 <sup>ii</sup>	2.449 (4)	Si1—O3	1.635 (5)
Ca—O1	2.557 (2)	Si1—O2	1.664 (2)
Ca—O2 <sup>iv</sup>	2.606 (3)	Si2—O6	1.593 (4)
Mn—O3	1.906 (4)	Si2—O5	1.6031 (13)
Mn—O4 <sup>v</sup>	1.909 (4)	Si2—O2	1.640 (3)
Mn—O8	1.949 (5)	Si2—O7	1.642 (4)
Mn—O8 <sup>vi</sup>	1.951 (5)		
O3—Mn—O4 <sup>v</sup>	179.1 (3)	O1 <sup>vii</sup> —Mn—O1 <sup>viii</sup>	179.1 (2)
O3—Mn—O8	89.73 (16)	O1 <sup>ix</sup> —Si1—O4 <sup>x</sup>	114.1 (2)
O4 <sup>v</sup> —Mn—O8	89.97 (16)	O1 <sup>ix</sup> —Si1—O3	115.0 (3)
O3—Mn—O8 <sup>vi</sup>	90.51 (17)	O4 <sup>x</sup> —Si1—O3	110.88 (13)
O4 <sup>v</sup> —Mn—O8 <sup>vi</sup>	89.81 (16)	O1 <sup>ix</sup> —Si1—O2	101.23 (13)
O8—Mn—O8 <sup>vi</sup>	179.1 (2)	O4 <sup>x</sup> —Si1—O2	107.6 (3)
O3—Mn—O1 <sup>vii</sup>	87.33 (17)	O3—Si1—O2	107.0 (3)
O4 <sup>v</sup> —Mn—O1 <sup>vii</sup>	91.84 (15)	O6—Si2—O5	111.1 (2)
O8—Mn—O1 <sup>vii</sup>	99.16 (17)	O6—Si2—O2	112.1 (2)
O8 <sup>vi</sup> —Mn—O1 <sup>vii</sup>	81.73 (17)	O5—Si2—O2	105.51 (11)
O3—Mn—O1 <sup>viii</sup>	92.99 (16)	O6—Si2—O7	112.6 (2)
O4 <sup>v</sup> —Mn—O1 <sup>viii</sup>	87.85 (16)	O5—Si2—O7	109.7 (2)
O8—Mn—O1 <sup>viii</sup>	81.70 (17)	O2—Si2—O7	105.5 (3)
O8 <sup>vi</sup> —Mn—O1 <sup>viii</sup>	97.41 (16)		

Symmetry codes: (i)  $x-1/2, y-1/2, z$ ; (ii)  $x-1/2, y+1/2, z$ ; (iii)  $-x+1/2, y+1/2, -z+1$ ; (iv)  $x-1, y, z$ ; (v)  $x+1/2, y+1/2, z+1$ ; (vi)  $-x+3/2, y-1/2, -z+2$ ; (vii)  $x+1/2, y-1/2, z$ ; (viii)  $-x+1, y, -z+2$ ; (ix)  $x+1, y, z$ ; (x)  $-x+1, y+1, -z+1$ .

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O7—H1 $\cdots$ O6 <sup>xi</sup>	0.73 (6)	1.94 (6)	2.662 (4)	168 (8)
O8—H2 $\cdots$ O9	0.64 (6)	2.28 (6)	2.842 (4)	149 (9)
O9—H3 $\cdots$ O6	0.74 (8)	2.06 (8)	2.737 (6)	153 (7)
O9—H4 $\cdots$ O8	0.72 (6)	2.14 (6)	2.842 (4)	167 (9)

Symmetry code: (xi)  $-x+3/2, y-1/2, -z+1$ .