

Crystal structure of harstigitite, $\text{MnCa}_6\text{Be}_4[\text{SiO}_4]_2[\text{Si}_2\text{O}_7]_2(\text{OH})_2$

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Dedicated to Professor Dr. F. Liebau on the occasion of his 60th birthday

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Abstract. The structure of harstigitite, $\text{MnCa}_6\text{Be}_4[\text{SiO}_4]_2[\text{Si}_2\text{O}_7]_2(\text{OH})_2$ from Värmland, Sweden, is orthorhombic with space group *Pnam*, $a = 9.793(2)$, $b = 13.636(3)$, $c = 13.830(3)$ Å, $Z = 4$ and $D_x = 3.19$ g cm⁻³. It was refined to R (unweighted) = 0.053 and R (weighted) = 0.050 using 3630 non-equivalent reflections. Harstigitite is a mixed-anion silicate which contains $[\text{SiO}_4]$ tetrahedra (mean Si–O distance 1.637 Å), $[\text{Si}_2\text{O}_7]$ groups (mean Si–O distance 1.623 Å), and in addition $[\text{Be}(\text{O},\text{OH})_4]$ tetrahedra (mean Be–(O,OH) distance 1.651 Å), $[\text{MnO}_6]$ polyhedra (mean Mn–O distance 2.222 Å) and $[\text{CaO}_8]$ polyhedra (mean Ca–O distance 2.507 Å). The ratio of single tetrahedra $[\text{SiO}_4]$ to double tetrahedra $[\text{Si}_2\text{O}_7]$ in the structure is 1:1.

Introduction

Harstigitite is a rare mineral which Moore (1968) suggested to have $[\text{Si}_3\text{O}_{10}]$ groups. Therefore, it was classified with aminoffite in the melilite group. No crystal structure determination has been published up to now.

Experimental

Crystals investigated in the present study were colourless, transparent fragments from Harstigen mine, Sweden. A crystal measuring

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Table 1. Positional and thermal ($\times 10^4$) parameters with standard deviations. The anisotropic temperature factors have the form $\exp\{-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*)\}$. The standard deviations in parentheses refer to the last digit.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn	0.9993(1)	0.3950(1)	0.2500	76(3)	81(3)	164(3)	0	0	-1(3)
Ca(1)	0.9962(1)	0.6083(0)	0.3859(1)	66(2)	76(2)	93(2)	-13(2)	-12(2)	-4(2)
Ca(2)	0.5086(1)	0.3157(0)	0.3876(1)	60(2)	94(2)	85(2)	-20(2)	6(2)	12(2)
Ca(3)	0.5004(1)	0.5897(0)	0.3926(0)	66(2)	74(2)	85(2)	-7(2)	-26(2)	16(2)
Si(1)	0.2281(1)	0.2579(1)	0.2500	39(5)	45(5)	83(5)	0	0	-1(4)
Si(2)	0.2831(1)	0.5151(1)	0.2500	20(4)	55(5)	45(4)	0	0	-1(4)
Si(3)	0.2142(1)	0.5498(1)	0.5490(1)	47(3)	39(3)	73(4)	12(3)	6(3)	9(3)
Si(4)	0.2325(1)	0.7485(1)	0.4521(1)	35(3)	47(3)	74(3)	-3(3)	10(3)	2(3)
Be(1)	0.2381(5)	0.4017(4)	0.4159(3)	95(18)	79(16)	72(16)	12(15)	-9(14)	21(15)
Be(2)	0.2624(7)	0.5394(5)	0.7500	26(23)	70(24)	192(31)	0	0	15(20)
Be(3)	0.2657(7)	0.7284(4)	0.2500	78(24)	50(22)	1(18)	0	0	2(18)
O(1)	0.1579(3)	0.6590(2)	0.5144(2)	63(9)	67(10)	128(11)	31(8)	11(8)	8(8)
O(2)	0.3952(2)	0.7417(2)	0.4549(2)	44(8)	71(9)	124(10)	14(8)	-5(8)	-8(8)
O(3)	0.1701(2)	0.8459(2)	0.5036(2)	54(9)	84(10)	92(10)	-28(8)	17(8)	-2(8)
O(4)	0.1675(3)	0.7400(2)	0.3458(2)	64(9)	133(11)	55(8)	-13(8)	5(7)	-29(8)
O(5)	0.1373(3)	0.4746(2)	0.4765(2)	68(9)	55(9)	81(9)	-51(8)	-11(8)	3(7)
O(6)	0.1529(2)	0.5308(2)	0.6577(2)	31(9)	91(10)	113(10)	4(8)	-2(8)	0(7)
O(7)	0.3778(2)	0.5504(2)	0.5471(2)	46(9)	61(9)	90(9)	-4(7)	4(7)	6(8)
O(8)	0.1602(3)	0.3165(2)	0.3434(2)	92(9)	40(8)	65(8)	-11(7)	-3(8)	-11(7)
O(9)	0.3425(3)	0.4606(2)	0.3460(2)	75(9)	38(8)	75(9)	10(7)	-21(7)	-13(7)
O(10)	0.1172(4)	0.5239(3)	0.2500	25(12)	137(15)	93(13)	0	0	-14(12)
O(11)	0.1590(4)	0.1485(3)	0.2500	52(13)	66(13)	109(14)	0	0	51(11)
O(12)	0.3926(3)	0.2476(3)	0.2500	43(12)	64(12)	87(12)	0	0	35(11)
O(13)	0.3507(3)	0.6245(3)	0.2500	15(11)	64(12)	120(14)	0	0	16(10)
O(14)	0.3666(4)	0.4499(3)	0.7500	111(15)	86(13)	69(13)	0	0	9(12)
O(15)	0.1115(5)	0.3146(3)	0.7500	105(16)	72(14)	176(17)	0	0	75(13)
H(1)	0.176(12)	0.883(8)	0.250	810(41)					

Table 2. Microprobe analysis of the harstigitite.

	Experimental (wt-%)	Theoretical (wt-%)
SiO ₂	40.44	40.60
CaO	36.21	37.89
MnO	6.48	7.99
BeO	—	11.27
H ₂ O	—	2.25
Total	83.13	100.00

0.050 × 0.200 × 0.200 mm was used for data collection on an automatic Philips PW 1100 four-circle diffractometer with graphite-monochromatized MoK α radiation ($\lambda = 0.7107 \text{ \AA}$) and ω -2 θ scan ($\theta_{\text{max}} = 40^\circ$). The intensities of 11 234 reflections were recorded. Symmetry equivalent intensities were averaged to give 5617 non-equivalent reflections; 3630 of them had $I \geq 3 \sigma(I)$ and were used for the subsequent refinement. The standard deviations, $\sigma(I)$, were estimated using the formula cited by Stout and Jensen (1968). Refined cell dimensions as given in the abstract were determined with the program LAT written by Hornstra and Vossers (1973/74) using 48 reflections. Lorentz and polarization corrections were applied. Absorption was not corrected. The positions of the heavy atoms were determined with MULTAN-78 (Main et al., 1978) and refined by full-matrix least-squares analyses with SHELX-76 (Sheldrick, 1976). The atomic scattering factors for Mn, Ca, Be were taken from the International Tables for X-ray Crystallography, Vol. IV, 1974, for neutral atoms and for Si, O by Cromer and Mann (1968). Anisotropic refinements of the crystal structure converged at R (unweighted) = 0.053 and R (weighted) = 0.050. $\{R(\text{weighted}) = [\sum w(|F_o| - |F_c|)^2]^{1/2} / (\sum w F_o^2)^{1/2}, w = 1/\sigma^2\}$. Final atomic parameters are given in Table 1, and microprobe analyses in Table 2. Lists of observed and calculated structure factors, bond lengths and angles have been deposited¹.

Description of the structure and results

The structure of harstigitite, MnCa₆Be₄[SiO₄]₂[Si₂O₇]₂(OH)₂, is depicted in Figure 1. Harstigitite contains [SiO₄] tetrahedra, [Si₂O₇] groups, [Be(O,OH)₄] tetrahedra, [MnO₆] polyhedra and [CaO₈] polyhedra. Si—O distances vary between 1.596 Å and 1.663 Å (mean 1.623 Å), Be—(O,OH)

¹ Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 51 365, the names of the authors and the title of the paper.

Table 3. Valence bond analysis.

	Si(1)	Si(2)	Si(3)	Si(4)	Be(1)	Be(2)	Be(3)	Mn	Ca(1)	Ca(2)	Ca(3)	Σ	
O(1)			0.91	0.90					0.25	0.06		2.12	O ²⁻
O(2)				1.08					0.26	0.24	0.26	1.84	O ²⁻
O(3)				0.99	0.52					0.36	0.29	2.16	O ²⁻
O(4)				1.05			0.49 × 2		0.22		0.08	1.84	O ²⁻
O(5)			1.01		0.51				0.20			1.90	O ²⁻
O(6)			0.96			0.46 × 2		0.32 × 2	0.18			2.00	O ²⁻
O(7)			1.06						0.26				
O(8)	0.91 × 2				0.41			0.25 × 2		0.38	0.31	1.87	O ²⁻
O(9)		0.99 × 2			0.52					0.23	0.29	1.97	O ²⁻
O(10)		0.98						0.43	0.24			1.65	O ²⁻
O(11)	0.96					0.45				0.27		1.68	O ²⁻
O(12)	1.02							0.32		0.31		1.65	O ²⁻
O(13)		0.98					0.49				0.24	1.71	O ²⁻
O(14)						0.55					0.29	0.84	OH ⁻
O(15)							0.44		0.31			0.75	OH ⁻
Σ	3.80	3.94	3.94	4.02	1.96	1.92	1.91	1.89	1.92	2.09	1.99		

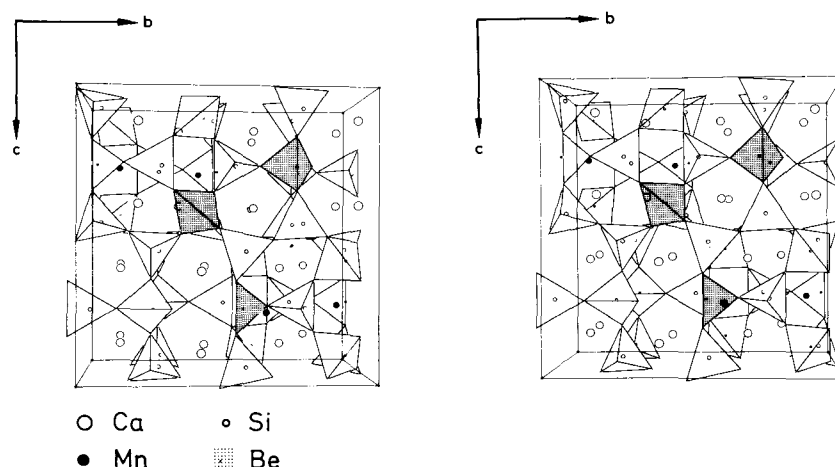


Fig. 1. Stereoscopic view of the unit cell as seen down the a axis.

distances between 1.600 Å and 1.713 Å (mean 1.651 Å), Mn–O distances between 2.104 Å and 2.301 Å (mean 2.222 Å) and Ca–O distances between 2.322 Å and 3.010 Å (mean 2.507 Å). According to Liebau's classification of silicates (Liebau, 1985) harstigitite is a new example of a mixed-anion silicate with $[\text{SiO}_4]$ single tetrahedra and $[\text{Si}_2\text{O}_7]$ double tetrahedra. Including the $[\text{Be}(\text{O},\text{OH})_4]$ tetrahedra, harstigitite contains loop-branched sechser single layers of corner-linked tetrahedra. In contrast to the classification of Moore (1968), it belongs to the epidote group. The tetrahedra form four-membered, five-membered, and eight-membered rings which, connected with one another, give rise to layers of composition $\text{Be}_8[(\text{SiO}_4)]_4[(\text{Si}_2\text{O}_7)]_4(\text{OH})_4$ parallel to (100). These layers are held together by the Ca and Mn ions which occur between them. Three of the oxygen atoms that form the Be(2) and Be(3) tetrahedra are shared with Si tetrahedra and two OH groups labelled O(14) and O(15), complete the Be tetrahedra. The presence of OH groups at these locations shows up from a difference Fourier synthesis and a valence bond analysis as described by Brown and Altermatt (1985) (see Table 3).

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