Effenbergerite, BaCu[Si$_4$O$_{10}$], a new mineral from the Kalahari Manganese Field, South Africa: description and crystal structure

G. GIESTER AND B. RIECK

Institut für Mineralogie und Kristallographie, Universität Wien, Dr. Karl Lueger-Ring 1,
A-1010 Wien, Austria

Abstract

Effenbergerite, ideally BaCu[Si$_4$O$_{10}$], structure determined by single crystal X-ray methods in space group $P4/ncc$, $a = 7.442(2)$Å, $c = 16.133(5)$Å, $V = 893.50$ Å^3, $Z = 4$, is a new mineral from the Wessels mine, Kalahari Manganese Field, South Africa. It is associated with native copper, calcite, quartz and clinozoisite within pectolite veinlets, embedded in a matrix of braunite, sugilite and hausmannite. Effenbergerite occurs as transparent blue platelets with perfect cleavage parallel to {001} in sizes up to $8.0 \times 8.0 \times 0.1$mm. It has a pale blue streak, subconchoidal fracture, a calculated density of 3.52gcm^{-3} and an estimated Mohs' hardness of 4–5. Effenbergerite is uniaxial negative with $\omega = 1.633(2)$, $\epsilon = 1.593(2)$, strongly pleochroic from intense blue (ω) to nearly colourless (ϵ). The strongest lines in the X-ray powder diffraction pattern (with refined lattice parameters $a = 7.440(1)$Å, $c = 16.133(2)$Å) are: ($d_{obs}/I_{obs}/hkl$) (8.0624/100/002), (4.0325/39/004), (3.5443/29/104), (3.1998/44/114), (2.6892/21/006), (2.3943/41/116), (2.0169/34/008), (1.9466/22/108) and (1.4802/21/2.0.70).

Effenbergerite is the natural analogue to synthetic BaCu[Si$_4$O$_{10}$], isotypic with SrCu[Si$_4$O$_{10}$] and CaCr[Si$_4$O$_{10}$] as well as with the minerals cuprorivaite, CaCu[Si$_4$O$_{10}$] and gillespite, BaFe[Si$_4$O$_{10}$]. The structure consists of silicate sheets [Si$_8$O$_{20}$]$^{8-}$ parallel (001) formed by corner-linkage of silicate 4-membered rings. The copper(II) atom is nearly planar 4-coordinated; the barium atom has a distorted cubelike environment of oxygen atoms. The mineral is named for Dr. Herta S. Effenberger of the University of Vienna, Austria.

KEYWORDS: effenbergerite, BaCu[Si$_4$O$_{10}$], barium copper silicate, new mineral, crystal structure, Kalahari Manganese Field, South Africa.

Introduction

A new mineral species was noticed on a sugilite specimen from the central-eastern orebody of the Wessels mine during a field trip in South Africa. Its perfect cleavage combined with its azure blue colour did not match the features of any mineral known to occur in the Kalahari Manganese Field. The subsequent investigation of the material revealed the first natural occurrence of the barium copper silicate compound synthesized and described by Pabst (1959). The authors have decided to name the new mineral effenbergerite in honour of Dr. Herta S. Effenberger, mineralogist and crystallographer at the University of Vienna, Austria. She has dedicated a major part of her scientific work to the stereochemistry of divalent copper, resulting in numerous crystal structure determinations, including many minerals, some of which were new species. The new mineral and the name have been approved by the I.M.A. Commission on New Minerals and Mineral Names. Portions of the type specimen are preserved in the collections of the Institut für Mineralogie und Kristallographie, University of Vienna under catalogue number 8H/01-060#1 and of the Smithsonian Institution, Washington DC under NMNH 170945.

Occurrence and paragenesis

Effenbergerite originates from the central-eastern orebody of the Wessels mine in the Kalahari Manganese Field, northwestern Cape Province, Republic of South Africa. The matrix consists primarily of braunite, sugilite and hausmannite. It is cut by pectolite veinlets, 0.1–1 mm wide, containing the new species here described, arranged more or less parallel to the walls of the veinlets, further abundant native copper, calcite, quartz, clinozoisite, as well as two unknown species. The mineral assemblage is believed to have formed as a result of a hydrothermal event, affecting the Kalahari Manganese Field 1300 million years ago, reaching maximum temperatures of 450°C (Kleyenstuber, 1984; Dixon, 1985, 1986). A more detailed account of the mineralogy of the Kalahari Manganese Field is given by Von Bezing et al. (1991).

Physical and optical properties

Effenbergerite is ditetragonal dipyramidal and occurs as subhedral plates with maximum dimensions 8 × 8 × 0.1mm. Its perfect cleavage parallel to {001} is always observable, a very poor cleavage parallel {110} is usually not readily recognized. Sometimes the forms {100}, {110}, and {102} are developed, whereas the form {001} is always present, at least as a cleavage plane. No twinning has been observed. The density of effenbergerite, measured by suspension of crystals in heavy liquids at room temperature, is 3.57(2) g cm^{-3}, which compares well with the calculated value of 3.52 g cm^{-3}, based on X-ray data. The slightly higher value can be attributed to microinclusions of native copper. Effenbergerite is brittle with subconchoidal fracture and a Mohs' hardness of $\approx$ 4–5. Its blue colour is almost that of linarite, the streak pale blue, the luster is vitreous on the cleavage planes, resinous on crystal faces and subvitreous on fracture surfaces. No fluorescence has been observed under either shortwave or longwave ultraviolet radiation. Effenbergerite is optically uniaxial negative with refractive indices, obtained with spindle stage methods, ω and ϵ = 1.633(2) and 1.593(2), respectively. The dispersion is weak with r > v. A strong pleochroism from intense blue in O and pale blue to colourless in E is observable. Inclusions of native copper are commonly seen within the crystals. Calculation of the Gladstone-Dale relationship using the constants of Mandarino (1981) yields a superior compatibility. Effenbergerite can be distinguished from all other blue minerals known thus far from the Wessels mine by its perfect cleavage and its insolubility in all commonly employed acids, except hydrofluoric acid.

Chemistry

The chemical composition of effenbergerite was obtained from energy-dispersive X-ray analysis (EDX) performed on a scanning electron microscope (SEM) Jeol JSM-6400, controlled by the program system LINK eXL10. An operating voltage of 20 kV was used; data were automatically corrected for attenuation and enhancement effects. The internal standards used are based on $BaSO_4$, $Cu_{met.}$, Al_2O_3 and SiO_2. Analysis on 14 crystal plates (27 different spots) yielded the composition (wt.%) of major components BaO = 32.48 (30.41–33.77), CuO = 16.52 (15.24–17.73), SiO_2 = 50.76 (48.84–53.53) with standard deviations (relative wt.%) of the single measurement about 1.3 for BaO, 2.8 for CuO and 0.8 for SiO_2. The empirical formula (based on 10 oxygen atoms p.f.u.) is $Ba_{1.00}Cu_{0.98}[Si_{3.99}O_{10}]$. The theoretical values for ideal $BaCu[Si_4O_{10}]$ are BaO: 32.40, CuO: 16.81, SiO_2: 50.79. On four cleavage plates Al was measured 0.5(2) (0.4–0.7 wt.% Al_2O_3) above 2σ limit; otherwise no further elements could be detected.

In addition, microprobe analyses were done with an ARL-SEMQ electron microprobe for minor elements. Operation conditions were 15 kV acceleration potential and about 15 nA sample current. Counting times for peak and background positions were 20s and 2 × 10s, respectively. 16 measurements yielded CaO, SrO and FeO < 0.02 wt.% and Al_2O_3 contents of 0.38(3), confirming the EDX analysis.

Infrared absorption spectra of 18 cleavage plates were measured on a FTIR spectrometer 1760X combined with a Perkin Elmer FTIR microscope, in the region from 6000 to 1000 cm^{-1}. 12 samples (4 of them tempered at 950°C) revealed no significant absorptions in the region of the OH fundamentals. Three crystals showed absorption bands centered at approx. 5200, 3500, and 1600 cm^{-1}, indicating the presence of H_2O. One of the samples showed an absorption band at 3300 cm^{-1} which is probably due to OH. Spot measurements revealed a strongly inhomogeneous distribution of 'water', ranging from significant absorption bands down to undetectable amounts within the respective cleavage plate. Quantitative contents for H_2O and OH cannot be derived from the IR measurements from the lack of available extinction coefficients, but based on rough estimations H_2O contents are probably < 0.1 wt%.

TABLE 1. Powder diffraction data for effenbergerite

d_{calc}	d_{obs}	I/I_o	h k l	d_{calc}	d_{obs}	I/I_o	h k l
8.0665	8.0624	100	0 0 2	1.4801	1.4802	21	2 0 10
5.4690	5.4653	1	1 0 2	1.4423	1.4417	2	3 2 8
5.2609	5.2575	1	1 1 0	1.3752	1.3750	3	2 2 10
4.4065	4.4033	10	1 1 2	1.3447	1.3445⎫		4 1 8
4.0332	4.0325	39	0 0 4	1.3444	1.3445⎭	11	0 0 12
3.5458	3.5443	29	1 0 4	1.3233	1.3230⎫		3 3 8
3.3781	3.3765	17	2 0 2	1.3230	1.3230⎭	3	1 0 12
3.2008	3.1998	44	1 1 4	1.3026	1.3026	2	1 1 12
3.0759	3.0786	6	2 1 2	1.2824	1.2821	2	5 1 6
2.8295	2.8295	1	2 1 3	1.2644	1.2648	1	2 0 12
2.7345	2.7347	13	2 0 4	1.2187	1.2186	1	4 0 10
2.6888	2.6892	21	0 0 6	1.1973	1.1976	7	5 0 8
2.6304	2.6305	4	2 2 0	1.1673	1.1676	2	3 1 12
2.5008	2.5008	2	2 2 2	1.1582	1.1582	4	4 2 10
2.3942	2.3943	41	1 1 6	1.1524	1.1523	4	0 0 14
2.2586	2.2582	2	3 1 2	1.1257	1.1256	5	1 1 14
2.2033	2.2021	2	2 2 4	1.1008	1.1009	1	2 0 14
2.1792	2.1777	1	2 0 6	1.0889	1.0888	2	2 1 14
2.0913	2.0911	2	2 1 6	1.0555	1.0557	1	2 2 14
2.0322	2.0333	6	3 1 4	1.0450	1.0452	1	3 0 14
2.0166	2.0169	34	0 0 8	1.0349	1.0352	3	3 1 14
1.9464	1.9466	22	1 0 8	0.9903	0.9901	4	1 1 16
1.8830	1.8832	13	1 1 8	0.9732	0.9730	2	2 0 16
1.8600	1.8611	3	4 0 0	0.9612	0.9617	1	7 3 3
1.7706	1.7708	10	3 1 6	0.9268	0.9266	2	3 1 16
1.7136	1.7144	1	3 3 2	0.9108	0.9107	1	5 4 11
1.6636	1.6628	1	4 2 0	0.9043	0.9039	1	5 1 14
1.6293	1.6288	2	4 2 2	0.8835	0.8835	2	1 1 18
1.6004	1.6005	2	2 2 8	0.8713	0.8715	2	2 0 18
1.5767	1.5768	2	1 0 10	0.8376	0.8376	1	3 1 18
1.5424	1.5427	3	1 1 10	0.8295	0.8295	1	5 1 16
1.5311	1.5310	4	3 1 8				

Equipment: Philips PW3020 diffractometer, ADS, sample spinner, graphite secondary monochromator, scintillation counter, CuK_α-radiation, 2–140° 2θ, silicon as internal standard.

Program: NBS*AIDS83 (Mighell *et al.*, 1981) for refinement of the lattice parameters: $a = 7.440(1)$Å, $c = 16.133(2)$Å. Comparison with a theoretical powder pattern (calculated on the crystal structure) reveals strong texture effects with a preferred orientation parallel to (001).

5.345 mg of effenbergerite were analysed with a computer controlled Mettler M3 microbalance combined with a TA 4000 Thermo Analysis System (TGA). Upon heating the sample to 500°C at 1°C min^{-1} and subsequent tempering at 950°C for one hour no significant loss of weight was found (< 0.5 wt.%). Tempered crystals remained transparent without any indication of decomposition.

The interpretation of these results is that in the cases where 'water' was observed, it is related predominantly to structurally bound H_2O-molecules (and subordinate to fluid inclusions), whereas minor (OH) might contribute to charge balance (partial substitution of Si^{4+} by Al^{3+}). As the incorporation of Al and H is only subordinate, the idealized formula of effenbergerite as nominally anhydrous $BaCu[Si_4O_{10}]$ seems to be justified. This is in accordance with the results of the crystal structure determination.

X-ray crystallography and structure determination

Single crystals of effenbergerite were preliminarily investigated using Weissenberg (unfiltered CuK_α) and precession (Zr-filtered MoK_α) methods, indicating that effenbergerite is tetragonal, space group $P4/ncc$, as known for the synthetic analogue

TABLE 2. Summary of crystal data, details of X-ray measurement and results of structure refinements

Effenbergerite	BaCu[Si$_4$O$_{10}$]
Space group	$P4/ncc$
a [Å]	7.442(2)
c [Å]	16.133(5)
c/a	2.168
V [Å^3]	893.50
Z	4
$\rho_{calc.}$ [g cm^{-3}]	3.52(1)
μ(Mo-K_α) [cm^{-1}]	73.4
Crystal dimensions [mm]	0.20 × 0.13 × 0.04
$(\sin\theta/\lambda)$ max [Å^{-1}]	0.7036
$h\ k\ l$ min/max	$-10/10$; $-10/10$; $-22/0$
Reflections measured	5584
Unique reflections	667
Reflections with $F_o > 4\sigma(F_o)$	586
2θ-range for lattice parameters [°]	32–36
Transmission factors	0.11 to 0.26
Extinction coefficient	0.0039(3)
Variable parameters	39
R1, wR2	0.014/0.041
$R1 = \Sigma \mid\mid F_o \mid - \mid F_c \mid\mid /\Sigma \mid F_o \mid$	
$wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$	
$w = 1/[\sigma^2(F_o^2) + 0.0261P^2]$	
$P = ([\text{max of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$	

Equipment: STOE four-circle diffractometer AED2; graphite monochromatized Mo-K_α radiation.

Data collection: 2θ-ω-scans, 40 steps/reflection, increased for α_1-α_2 dispersion, 2*5 steps for background correction, 0.03° and 1.0–4.0 s/step, standard reflections (008), (420), (240) each 120 min.

Program used for structure refinement: SHELXL-93 (Sheldrick, 1993).

(Pabst, 1959; Lin *et al.*, 1992; Janczak and Kubiak, 1992; Chakoumakos *et al.*, 1993). The cell parameters were obtained by least-squares treatment of powder data with silicon as internal standard; the powder diffraction data are listed in Table 1, as well as from accurately measured 2θ values of 48 reflections, automatically determined on a four-circle diffractometer. The values obtained are consistent within the limits of one standard deviation. For structure determination an appropriate single-crystal cleavage plate was selected by microscopic examination with polarized light, and X-ray film work. In all our investigations no twinning was observed, but most samples showed subparallel intergrowth resulting in diffuse X-ray diffraction spots. Crystal data, technical details of the data collection and of the structure refinements are given in Table 2. The X-ray intensities were corrected for Lorentz and polarization effects, as well as for absorption according to the crystal shape (ψ-scans). The structure refinement was started with the parameters of gillespite as given by Hazen and Burnham (1974). Complex scattering curves for neutral atoms were taken from the International Tables for X-ray Crystallography; Wilson (1992). Refined structural parameters, as obtained by full-matrix least-squares techniques on F^2, are listed in Table 3. Residual electron densities in a final difference Fourier map were <0.5e Å^{-3}. Selected interatomic bond distances and angles are given in Table 4. The crystal structure determination confirmed isotypy with the synthetic compounds BaCu[Si$_4$O$_{10}$], SrCu[Si$_4$O$_{10}$] and CaCr[Si$_4$O$_{10}$] (Pabst, 1959; Lin *et al.*, 1992; Janczak and Kubiak, 1992; Chakoumakos *et al.*, 1993; Belsky *et al.*, 1984) as well as with the minerals cuprorivaite, CaCu[Si$_4$O$_{10}$], (Pabst, 1959) and gillespite, BaFe[Si$_4$O$_{10}$], (low-pressure phase gillespite I, Hazen and Burnham, 1974; Hazen and Finger, 1983).

TABLE 3. Structural parameters of effenbergerite with e.s.d.'s in parentheses. U_{ij} are given in pm^2. The anisotropic displacement factor is defined as $exp[-2\pi^2\Sigma_i\Sigma_j U_{ij}h_ih_ja_i^*a_j^*]$

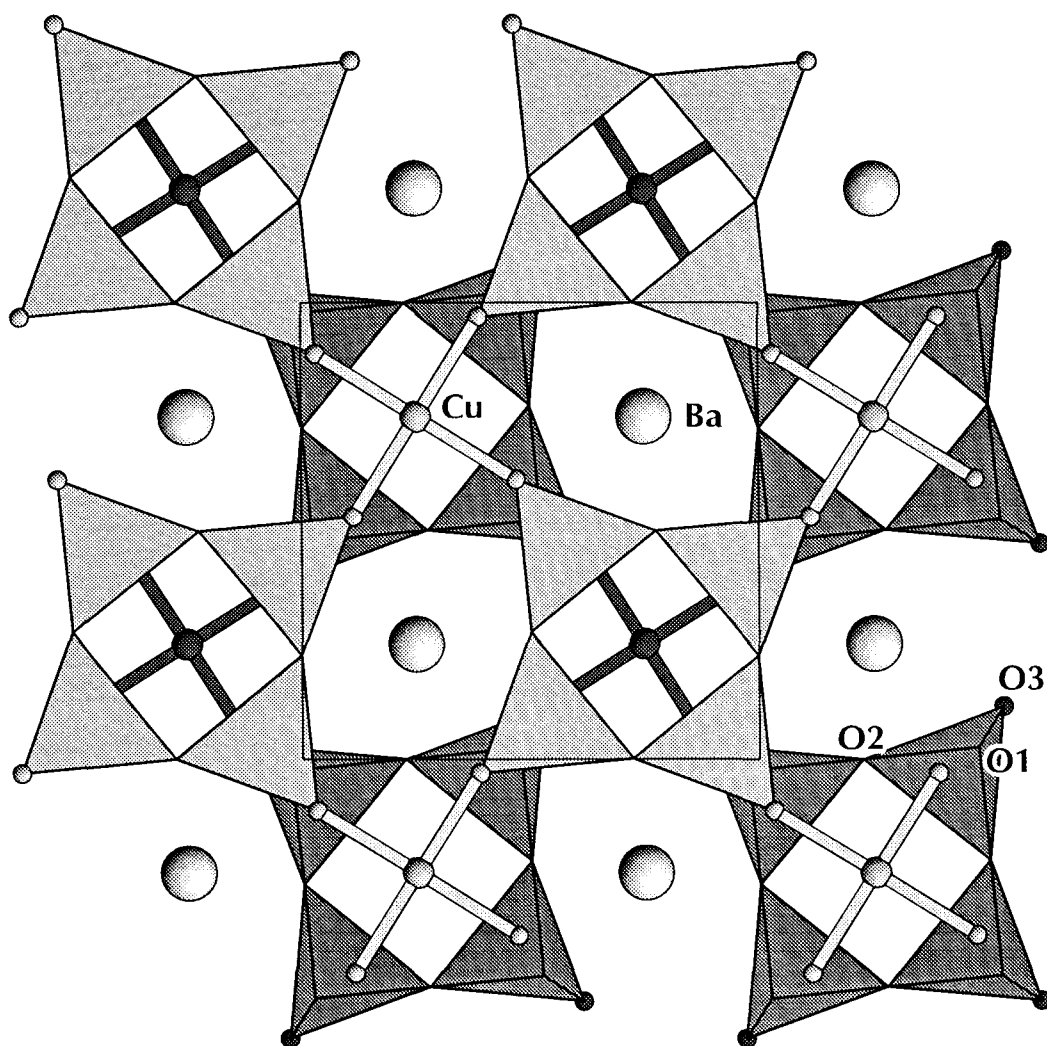|	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{equ}
Cu	¼	¼	0.09448(3)	78(1)	78(1)	146(2)	0	0	0	101(1)
Ba	¼	¾	0	154(1)	154(1)	98(1)	0	0	0	135(1)
Si	0.51860(5)	0.93877(6)	0.15462(3)	88(2)	91(2)	109(2)	−12(1)	10(1)	−1(1)	96(1)
O1	0.4758(3)	0.9758(3)	1/4	403(8)	403(8)	188(11)	−131(7)	131(7)	−93(10)	331(6)
O2	0.7244(1)	0.9991(2)	0.1364(1)	100(5)	264(6)	212(7)	58(6)	−7(4)	−16(4)	192(3)
O3	0.3877(2)	0.0311(1)	0.0903(1)	181(6)	115(5)	300(7)	−25(5)	−96(5)	56(4)	199(3)

FIG. 1. Structural detail of effenbergerite (single sheet) in projection parallel to [001]. The Ba atoms, positioned between the sheets, are indicated as large circles. The figure was drawn with the program ATOMS (Dowty, 1993).
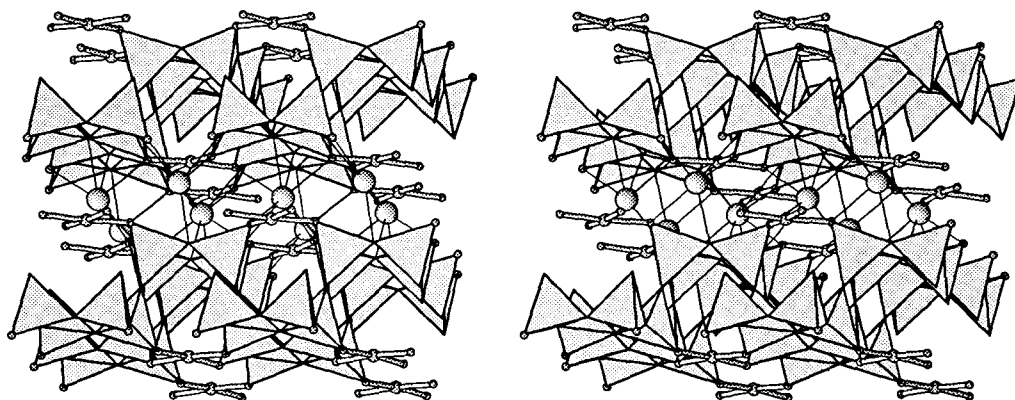
FIG. 2: Stereoplot of the crystal structure of effenbergerite in projection parallel to [100].

Crystal structure

Effenbergerite is an anhydrous sheet silicate containing unbranched single layers (cf. Liebau, 1985) with four-membered rings [Si_4O_{12}] with symmetry 4 as the basic silicate complex (Figs. 1, 2): four SiO_4 tetrahedra are corner-linked by each two oxygen atoms O2 to form the ring, one oxygen

(O1) of each tetrahedron belongs to a neighbouring 4-membered unit. The SiO_4 tetrahedron is moderately distorted with Si—O distances ranging from 1.58–1.63Å. All O1 atoms of the ring point to the same direction of the c-axis. This orientation is reverse to that of all four adjacent rings; thus an infinite buckled sheet [Si_8O_{20}]$^{8-}$ parallel to (001) is formed.

TABLE 4. Interatomic bond lengths [Å], bond angles [°] (with e.s.d.'s in parentheses) and intrapolyhedral O-O distances (given in brackets) for effenbergerite

		[°]	[Å]
Cu–O3	4x		1.925(1)
O3–Cu–O3	4x	89.93(5)	[2.721(2)]
Ba–O3	4x		2.748(1)
Ba–O2	4x		2.893(1)
< Ba–O >			< 2.821 >
Si–O3	1x		1.581(1)
Si–O1	1x		1.595(1)
Si–O2	1x		1.623(1)
Si–O2	1x		1.627(1)
< Si–O >			< 1.607 >
O3–Si–O1	1x	115.8(1)	[2.690(2)]
O3–Si–O2	1x	110.1(1)	[2.625(2)]
O3–Si–O2	1x	105.0(1)	[2.545(2)]
O1–Si–O2	1x	108.4(1)	[2.610(2)]
O1–Si–O2	1x	109.1(1)	[2.625(2)]
O2–Si–O2	1x	108.3(1)	[2.635(2)]
< O–Si–O >		< 109.4 >	< 2.622 >

TABLE 5. Selected interatomic distances [Å] and lattice parameters for effenbergerite and related Me1Me2[Si$_4$O$_{10}$] compounds. Aplanarity [Å] defined as elevation of the Me2 atom above the plane of the O3 atoms

Me1,Me2	Ba,Cu	Ba,Cu	Ba,Cu	Ba,Cu	Sr,Cu	Ca,Cu	Ca,Cu	Ba,Fe	Ca,Cr
References	*1*	*2*	*3*	*4*	*2*	*2*	*5*	*6*	*7*
Me1-O3	2.748(1)	2.748(2)	2.749(4)	2.755(3)	2.536(1)	2.373(1)	2.45(4)	2.747(2)	2.360(1)
Me1-O2	2.893(1)	2.898(2)	2.889(4)	2.900(3)	2.761(2)	2.654(2)	2.70(4)	2.925(2)	2.698(1)
<Me1[8]–O>	2.821	2.823	2.819	2.828	2.648	2.513	2.575	2.836	2.529
Me2[4]-O3	1.925(1)	1.920(2)	1.922(4)	1.918(3)	1.921(1)	1.929(1)	1.91(4)	1.985(2)	2.000(1)
aplanarity	0.067	0.071	0.056	0.058	0.028	−0.003	0.0	0.027	−0.036
Si-O3	1.581(1)	1.587(3)	1.571(4)	1.581(3)	1.585(3)	1.588(2)	1.59(4)	1.578(2)	1.581(1)
Si-O1	1.595(1)	1.591(3)	1.596(4)	1.595(1)	1.594(2)	1.601(2)	1.60(4)	1.594(1)	1.601(1)
Si-O2	1.623(1)	1.620(3)	1.624(4)	1.620(4)	1.626(3)	1.619(3)	1.59(4)	1.620(2)	1.623(1)
Si-O2	1.627(1)	1.629(3)	1.626(4)	1.633(3)	1.631(2)	1.630(2)	1.60(4)	1.627(2)	1.629(1)
<Si–O>	1.607	1.606	1.604	1.607	1.609	1.609	1.595	1.605	1.609
a_0[Å]	7.442(2)	7.4409(3)	7.440(2)	7.447(1)	7.3707(2)	7.3017(3)	7.30(1)	7.5161(3)	7.378(5)
c_0[Å]	16.133(5)	16.1367(8)	16.097(6)	16.138(2)	15.5904(6)	15.1303(6)	15.12(2)	16.0759(7)	15.119(2)
V[Å^3]	893.5	893.4	891.0	895.0	846.9	806.7	805.7	908.2	823.0

References: (1) this study; (2) Chakoumakos *et al.* (1993); (3) Lin *et al.* (1992); (4) Janczak and Kubiak (1992); (5) Pabst (1959); (6) Hazen and Finger (1983); (7) Belsky *et al.* (1984).

O1 is bonded to two Si atoms only (Si-O1-Si:177.8°), O2 to two Si atoms and one Ba atom, and O3 to each one Si, Cu and Ba atom. The surrounding of O2 is almost planar (sum of the bond angles 359.8°), that of O3 slightly pyramidal (sum of the bond angles 354.3°).

The copper atom (site symmetry 4) is in square, nearly planar coordination (aplanarity 0.067Å) with O3 atoms belonging to four rings. Geometry and a Cu–O distance of 1.925Å compare well with common experience for 4-coordinated divalent copper (< 1.930Å >, Lambert, 1988). Next oxygen neighbours are as far as 3.65Å. The barium atom (site symmetry 4̄) is bound to eight oxygen atoms (distorted cube) with additional oxygens > 3.47Å. These sheets are interconnected via BaO$_8$ polyhedra only, resulting in a perfect cleavage parallel to (001).

Table 5 gives a short comparison of structural details for effenbergerite and isotypic compounds proving them to be quite similar in respect to linkage and distortion of the coordination polyhedra. It has to be noted that the planar 4-coordination of the Me2 atom, while often observed for Cu(II), is rather unusual for ferrous iron. Furthermore, the compounds CaMe2[Si$_4$O$_{10}$] Me2 = Mn,Co,Ni are mentioned in the literature (Nicolini and Porta, 1970). Based on X-ray powder patterns these three compounds were assigned to the space group *P*4/*ncc* by Nicolini and Porta. Although the cell parameters are similar to CaCu[Si$_4$O$_{10}$], the authors infer from the results of magnetic and X-ray diffraction measurements that the Mn, Co and Ni compounds have a different crystal structure than CaCu[Si$_4$O$_{10}$].

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