

Crystal chemistry of silica-rich Barium silicates

I: Refinement of the crystal structures of $\text{Ba}_4[\text{Si}_6\text{O}_{16}]$, $\text{Ba}_5[\text{Si}_8\text{O}_{21}]$
and $\text{Ba}_6[\text{Si}_{10}\text{O}_{26}]$, silicates with triple, quadruple and quintuple chains

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Abstract. The crystal structures of the three synthetic title compounds have been refined with three-dimensional $\text{MoK}\alpha$ X-ray intensities. For each compound results are given in the order a , b , c , β , Z , space group, number of independent reflections, R (unweighted), R (weighted):

$\text{Ba}_4[\text{Si}_6\text{O}_{16}]$: 12.477(2) Å, 4.685(1) Å, 13.944(3) Å,
93.54(2)°, 2, $P2_1/c$, 1249, 0.051, 0.046.

$\text{Ba}_5[\text{Si}_8\text{O}_{21}]$: 32.675(7) Å, 4.695(1) Å, 13.894(3) Å,
98.10(2)°, 4, $C2/c$, 915, 0.053, 0.044.

$\text{Ba}_6[\text{Si}_{10}\text{O}_{26}]$: 20.196(4) Å, 4.707(1) Å, 13.842(3) Å,
98.61(2)°, 2, $P2_1/c$, 1529, 0.058, 0.048.

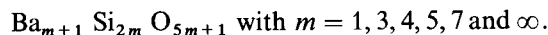
In the three silicates corner-sharing $[\text{SiO}_4]$ tetrahedra form chains with two tetrahedra in the repeat unit parallel $[010]$ (*zweier* single chains). In $\text{Ba}_4[\text{Si}_6\text{O}_{16}]$ three such single chains are linked into a *zweier* triple chain, in $\text{Ba}_5[\text{Si}_8\text{O}_{21}]$ four chains make a *zweier* quadruple chain and in $\text{Ba}_6[\text{Si}_{10}\text{O}_{26}]$ five chains make a *zweier* quintuple chain. Each barium ion is coordinated by eight oxygen atoms forming distorted square antiprisms.

Introduction

The partial system $\text{BaSiO}_3 - \text{SiO}_2$ has been the subject of intensive studies. The existence of a series of phases has been reported:

The low-temperature (l) and the high-temperature (h) phases $\text{BaO} \cdot \text{SiO}_2$ (l) and (h) (Liebau, 1960), $2 \text{BaO} \cdot \text{SiO}_2$ (l) and (h), $5 \text{BaO} \cdot 8 \text{SiO}_2$ (l) and (h), $3 \text{BaO} \cdot 5 \text{SiO}_2$ (Oehlschlegel, 1971) and $4 \text{BaO} \cdot 7 \text{SiO}_2$ (Segnit and Stevens, 1970) and $\text{BaO} \cdot 2 \text{SiO}_2$ (l) and (h) (Rogers, 1932; Roth and Levin, 1959).

All these compounds can be regarded as members of a homologous series of phases with the general formula



Of particular interest are the disputed regions of solid solution between $\text{BaO} \cdot \text{SiO}_2$ and $2 \text{BaO} \cdot 3 \text{SiO}_2$, and between $2 \text{BaO} \cdot 3 \text{SiO}_2$ and $\text{BaO} \cdot 2 \text{SiO}_2$ which was reported by Eskola (1922), Levin and Ugrinic (1953), Dietzel, Wickert and Köppen (1954) and Grebenschchikov and Toropov (1962), but rejected by Roth and Levin (1959), Mac Dowell (1965), Oehlschlegel (1971) and Gunawardane and Glasser (1974). While $\text{BaO} \cdot \text{SiO}_2$ (l) is isostructural with SrGeO_3 (Hilmer, 1963) and is therefore a cyclotrisilicate with ring anions $[\text{Si}_3\text{O}_9]$, $\text{BaO} \cdot \text{SiO}_2$ (h) is a polysilicate, $\text{Ba}_2[\text{Si}_2\text{O}_6]$, with *zweier*¹ single chains, i.e. with single chains having two corner-shared $[\text{SiO}_4]$ tetrahedra in the repeat unit (Grosse and Tillmanns, 1974). Toropov et al. supposed that in $2 \text{BaO} \cdot 3 \text{SiO}_2$, $5 \text{BaO} \cdot 8 \text{SiO}_2$ and $3 \text{BaO} \cdot 5 \text{SiO}_2$ three, four and five *zweier* single chains respectively are linked to *zweier* triple, quadruple and quintuple chains respectively (Lasarev, Tenisheva and Grebenschchikov, 1961; Grebenschchikov and Toropov, 1962). This was verified with two-dimensional structure analyses by Katscher and Liebau (1965, 1966). Both $\text{BaO} \cdot 2 \text{SiO}_2$ (l), known as the mineral sanbornite, and $\text{BaO} \cdot 2 \text{SiO}_2$ (h) contain *zweier* single layers (Douglass, 1958; Katscher, Bissert and Liebau, 1973). The structural formulae of these silicates should, therefore, be written as $\text{Ba}_3^c[\text{Si}_3\text{O}_9]$, $\text{Ba}_{2\infty}^1[\text{Si}_2\text{O}_6]$, $\text{Ba}_4^3[\text{Si}_6\text{O}_{16}]$, $\text{Ba}_5^4[\text{Si}_8\text{O}_{21}]$, $\text{Ba}_6^5[\text{Si}_{10}\text{O}_{26}]$, $\text{Ba}_2^2[\text{Si}_4\text{O}_{10}]$ (l), and $\text{Ba}_2^2[\text{Si}_4\text{O}_{10}]$ (h) respectively (Liebau, 1972). Unexpectedly, a phase $\text{Ba}_3^2[\text{Si}_4\text{O}_{11}]$ with *zweier* double chains is still unknown while the existence of the phase $4 \text{BaO} \cdot 7 \text{SiO}_2$ described by Segnit and Stevens (1970) is still contested.

Since $\text{BaO} - \text{SiO}_2$ is the only binary silicate system in which a whole series of stable phases is known in the range $1 : 3 \leq \text{Si} : \text{O} \leq 1 : 2.5$ it is most suitable to study the crystal chemistry of condensation of silicate chains to single layers as well as the problem of solid solution between high-polymers. Unfortunately, $\text{Ba}_{2\infty}^1[\text{Si}_2\text{O}_6]$ (h) is the only one of these silica-rich barium silicates for which an accurate structure determination has been published. The structure of $\text{Ba}_4^3[\text{Si}_6\text{O}_{16}]$ has been refined with 1550 counter measured intensities by Filipenko et al. (1971) to $R = 0.08$, but the atomic distances within the $[\text{SiO}_4]$ tetrahedra show large variations which for some of the tetrahedra are outside the range found in accurately determined silicate structures. The structure determinations of the other phases have been done with photographically recorded two-dimensional intensity data only, so that accurate refinements are most desirable.

In order to solve the problems mentioned above we have refined the structures of the low-temperature phases of $\text{Ba}_{m+1}[\text{Si}_{2m}\text{O}_{5m+1}]$ ($m = 3, 4$

¹ The nomenclature and structural formulae used are those described by Liebau (1972)

and 5) and of the two $\text{Ba}_2[\text{Si}_4\text{O}_{10}]$ phases with three-dimensional diffractometer intensities and have undertaken a high-resolution electronmicroscopic study of the former. The results of these studies will be published in a series of papers of which this first one describes the structure refinements of the three barium silicates containing multiple chains. Part II will describe results of a high-resolution electron microscopy study of $\text{Ba}_{m+1}[\text{Si}_{2m}\text{O}_{5m+1}]$ crystals with $m = 3, 4$ and 5 ; Part III will be a report of structure refinements of $\text{Ba}_2[\text{Si}_4\text{O}_{10}]$ (l) and (h) while Part IV will give a detailed discussion of the crystal chemical relations between all these silica-rich barium silicates.

Experimental

Single crystals of the three phases $\text{Ba}_4[\text{Si}_6\text{O}_{16}]$, $\text{Ba}_5[\text{Si}_8\text{O}_{21}]$ and $\text{Ba}_6[\text{Si}_{10}\text{O}_{26}]$ were grown by heating tablets of stoichiometric mixtures of BaCO_3 and SiO_2 several days at 1400°C (Katscher, 1969). Refined cell dimensions (Table 1) were determined on an automatic Philips PW 1100 four-circle diffractometer

Table 1. Cell dimensions, space groups and details of the structure determination of barium silicates

	$\text{Ba}_2[\text{Si}_2\text{O}_6]$	$\text{Ba}_4[\text{Si}_6\text{O}_{16}]$	$\text{Ba}_5[\text{Si}_8\text{O}_{21}]$	$\text{Ba}_6[\text{Si}_{10}\text{O}_{26}]$
a [Å]	5.611(1)	12.477(2)	32.675(7)	20.196(4)
b [Å]	4.580(1)	4.685(1)	4.695(1)	4.707(1)
c [Å]	12.431(2)	13.944(3)	13.894(3)	13.842(3)
β [°]	90	93.54(2)	98.10(2)	98.61(2)
Z	2	2	4	2
Space group	$P2_12_12_1$	$P2_1/c$	$C2/c$	$P2_1/c$
ρ_c [g/cm ³]	4.44	3.97	3.93	3.88
	Phase			
	$\text{Ba}_4[\text{Si}_6\text{O}_{16}]$	$\text{Ba}_5[\text{Si}_8\text{O}_{21}]$	$\text{Ba}_6[\text{Si}_{10}\text{O}_{26}]$	
Size [mm]	$0.065 \times 0.040 \times 0.115$	$0.075 \times 0.050 \times 0.100$	$0.070 \times 0.075 \times 0.100$	
μ [cm ⁻¹]	103.2	100.1	97.7	
Number of non equivalent reflections with $ F_o > 3\sigma$	1249	915	1529	
R (unweighted)	0.051	0.053	0.058	
R (weighted)	0.046	0.044	0.048	
Parameters refined	52	67	84	

Table 2. Final fractional atomic coordinates and thermal parameters for Ba₄[Si₆O₁₆], Ba₅[Si₈O₂₁] and Ba₆[Si₁₀O₂₆]. Estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso} (Å ²)
Ba₄[Si₆O₁₆]				
Ba(1)	0.5820(1)	0.7730(3)	0.1116(1)	0.65(2)
Ba(2)	0.8552(1)	0.2537(4)	0.0323(1)	0.67(2)
Si(1)	0.6493(4)	0.8128(10)	0.3895(3)	0.43(8)
Si(2)	0.7241(4)	0.3204(11)	0.2770(3)	0.33(8)
Si(3)	0.9731(4)	0.3209(11)	0.3126(3)	0.36(8)
O(1)	0.5271(9)	0.7509(43)	0.4156(8)	0.92(19)
O(2)	0.7339(9)	0.7664(40)	0.4779(8)	0.89(21)
O(3)	0.6465(10)	0.1482(27)	0.3501(9)	0.88(22)
O(4)	0.6814(11)	0.6466(30)	0.2888(9)	0.94(24)
O(5)	0.7151(9)	0.2349(40)	0.1675(8)	0.91(21)
O(6)	0.8446(9)	0.3020(32)	0.3260(9)	1.09(24)
O(7)	0.0338(9)	0.2366(41)	0.4101(8)	0.87(21)
O(8)	0.0029(10)	0.6490(28)	0.2868(9)	0.74(22)
Ba₅[Si₈O₂₁]				
Ba(1)	0.2816(1)	0.5248(10)	0.1172(1)	0.65(4)
Ba(2)	0.3882(1)	0.0298(8)	0.0537(1)	0.70(4)
Ba(3)	0	0	0	0.76(5)
Si(1)	0.3073(2)	0.5431(22)	0.3969(5)	0.46(14)
Si(2)	0.3348(2)	0.0391(27)	0.2885(5)	0.53(16)
Si(3)	0.4284(3)	0.0690(18)	0.3383(6)	0.57(15)
Si(4)	0.4505(3)	0.5761(19)	0.2225(6)	0.54(16)
O(1)	0.2624(5)	0.5438(62)	0.4188(12)	0.43(39)
O(2)	0.3404(5)	0.4720(95)	0.4924(12)	0.42(39)
O(3)	0.3035(6)	0.8663(41)	0.3506(14)	0.65(35)
O(4)	0.3222(7)	0.3598(47)	0.3038(16)	0.99(43)
O(5)	0.3334(6)	0.0139(228)	0.1772(13)	1.39(47)
O(6)	0.3813(4)	0.0282(87)	0.3520(11)	0.30(35)
O(7)	0.4563(5)	0.0095(264)	0.4374(13)	0.73(43)
O(8)	0.4316(7)	0.4026(41)	0.3069(15)	1.20(42)
O(9)	0.4382(6)	0.9019(42)	0.2386(15)	0.57(38)
O(10)	0.4357(6)	0.4731(125)	0.1137(14)	1.03(50)
O(11)	0	0.5547(122)	$\frac{1}{4}$	3.50(98)
Ba₆[Si₁₀O₂₆]				
Ba(1)	0.9487(1)	0.7729(4)	0.3443(3)	0.70(3)
Ba(2)	0.7745(1)	0.2080(4)	0.2066(4)	0.77(3)
Ba(3)	0.5926(1)	0.7475(3)	0.0657(3)	0.77(3)
Si(1)	0.9071(3)	0.7943(17)	0.6077(14)	0.58(11)
Si(2)	0.8643(3)	0.2927(17)	0.4805(14)	0.57(11)
Si(3)	0.7141(3)	0.1794(16)	0.4619(14)	0.52(11)
Si(4)	0.6747(3)	0.6755(15)	0.3344(14)	0.23(11)
Si(5)	0.5170(3)	0.6757(16)	0.3174(14)	0.51(11)

Table 2 (Continued)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso} (Å ²)
Ba ₆ [Si ₁₀ O ₂₆]				
O(1)	0.9815(8)	0.7138(43)	0.6604(38)	0.78(30)
O(2)	0.8492(8)	0.7769(46)	0.6786(40)	0.65(31)
O(3)	0.9160(9)	0.1163(40)	0.5609(42)	1.20(33)
O(4)	0.8862(9)	0.6148(41)	0.5036(43)	0.93(34)
O(5)	0.7878(8)	0.2410(44)	0.5116(35)	0.69(28)
O(6)	0.8657(9)	0.2211(51)	0.3691(44)	1.21(35)
O(7)	0.6660(9)	0.2482(54)	0.5386(47)	1.10(37)
O(8)	0.7154(10)	0.8496(42)	0.4272(45)	1.53(36)
O(9)	0.6993(8)	0.3578(35)	0.3555(36)	0.19(28)
O(10)	0.6870(9)	0.7688(50)	0.2309(43)	0.91(34)
O(11)	0.5959(9)	0.6819(42)	0.3532(43)	1.45(34)
O(12)	0.4803(8)	0.7700(50)	0.4054(40)	0.79(32)
O(13)	0.5001(9)	0.3572(42)	0.2864(46)	1.46(36)

with the programm LAT written by Hornstra and Vossers (1973/74). They are given in Table 1 together with the values determined by Grosse and Tillmanns (1974) for Ba₂[Si₂O₆] (h).

Intensities were collected with the same diffractometer with MoK α radiation ($\lambda = 0.7107 \text{ \AA}$) and $\vartheta - 2\vartheta$ scan ($2^\circ \leq \vartheta \leq 30^\circ$). Due to the small size of the crystals (Table 1) only a rather limited number of non-equivalent reflections with $|F_o| > 3\sigma$ ($|F_o|$) could be measured for each phase, restricting the accuracy of the structural parameters determined.

The standard deviation, $\sigma(F_o)$, was estimated by

$$\sigma(F_o) = \frac{1}{2} \frac{k}{(LP)^{1/2}} \left[\frac{N_T + N_{bg1} + N_{bg2} + (0.01 N_{pk})^2}{N_T - N_{bg1} - N_{bg2}} \right]^{1/2}$$

(Stout and Jensen, 1968), where N_T is the total peak count and N_{bg1} and N_{bg2} are the background counts on both sides of the peak. N_{pk} is defined by $N_{pk} = N_T - N_{bg1} - N_{bg2}$. Lorentz, polarization and absorption correction (Busing and Levy, 1957) were applied.

Space group symmetry was deduced from systematic absences and, in the case of Ba₄[Si₆O₁₆], very strongly supported by the distribution of *E*-values as computed by MULTAN. Least squares refinements were started with approximate atomic coordinates determined by Filipenko et al. (1971) for Ba₄[Si₆O₁₆], by Katscher (1969) for Ba₅[Si₈O₂₁], and by Katscher and Liebau (1966) for Ba₆[Si₁₀O₂₆], the program systems SHELX-76 and X-RAY 73 were used for the refinement. Scattering factors for ionized atoms were taken from International Tables Vol. III (1962) and Vol. IV (1974). The final

$$\text{values of } R = [\Sigma ||F_o| - |F_c| | / \Sigma |F_o|] \text{ and } R_w = \left[\frac{\Sigma w (|F_o| - |F_c|)^2}{\Sigma w F_o^2} \right]^{1/2},$$

($w = 1/\sigma^2$), for isotropic refinement are given in Table 1, final atomic parameters in Table 2, bond lengths and bond angles in Tables 3, 4 and 5. A list of observed and calculated structure factors can be obtained from the authors.

Table 3. Interatomic distances (in Å) and bond angles (in °) in $\text{Ba}_4[\text{Si}_6\text{O}_{16}]$. (Standard deviations in parentheses.) O*: bridging oxygen atoms

[SiO ₄] tetrahedra					
Si—O distances		O—O distances	O—Si—O angles		
Si(1)—O(2)	1.59(1)	O(3)*—O(4)*	2.55(2)	99.4(0.7)	
—O(1)	1.62(1)	O(1)—O(3)*	2.59(2)	104.1(0.9)	
—O(3)*	1.66(1)	O(1)—O(2)	2.67(2)	113.0(0.7)	
—O(4)*	1.68(1)	O(2)—O(3)*	2.71(2)	112.6(0.8)	
mean	1.638	O(1)—O(4)*	2.74(2)	112.5(0.7)	
		O(2)—O(4)*	2.74(2)	113.9(0.7)	
		mean	2.667	mean	109.3
Si(2)—O(5)	1.58(1)	O(3)*—O(4)*	2.53(2)	100.9(0.7)	
—O(6)*	1.62(1)	O(4)*—O(5)	2.61(2)	109.3(0.8)	
—O(4)*	1.63(1)	O(3)*—O(6)*	2.62(2)	106.1(0.7)	
—O(3)*	1.66(1)	O(4)*—O(6)*	2.63(2)	108.0(0.7)	
mean	1.623	O(5)—O(6)*	2.67(2)	113.9(0.7)	
		O(3)*—O(5)	2.77(2)	117.6(0.8)	
		mean	2.638	mean	109.3
Si(3)—O(7)	1.57(1)	O(8)*—O(8)*	2.56(1)	102.6(0.7)	
—O(6)*	1.63(1)	O(6)*—O(7)	2.59(2)	108.3(0.7)	
—O(8)*	1.63(1)	O(7)—O(8)*	2.60(2)	109.0(0.8)	
—O(8)*	1.65(1)	O(6)*—O(8)*	2.64(2)	107.6(0.7)	
mean	1.620	O(6)*—O(8)*	2.64(2)	108.5(0.7)	
		O(7)—O(8)*	2.78(2)	120.3(0.8)	
		mean	2.635	mean	109.4
Si—O—Si angles					
Si(1)—O(3)*—Si(2)	131.4(0.9)				
Si(1)—O(4)*—Si(2)	128.1(0.8)				
Si(2)—O(6)*—Si(3)	147.9(0.9)				
Si(3)—O(8)*—Si(3)	134.8(0.9)				
mean	135.6				
[BaO ₈] polyhedra					
Ba(1)—O(1)	2.64(2)	Ba(2)—O(5)	2.65(1)		
—O(2)	2.75(1)	—O(7)	2.75(2)		
—O(4)*	2.76(1)	—O(2)	2.79(2)		
—O(1)	2.78(1)	—O(7)	2.88(1)		
—O(1)	2.81(2)	—O(6)*	2.88(1)		
—O(5)	2.81(2)	—O(7)	2.89(1)		
—O(3)*	2.99(1)	—O(2)	2.94(2)		
—O(5)	3.09(2)	—O(8)*	3.03(1)		
mean	2.83	mean	2.85		
All other Ba(1)—O > 3.80		All other Ba(2)—O > 3.55			

Table 4. Interatomic distances (in Å) and bond angles (in °) in Ba₅[Si₈O₂₁]. (Standard deviations in parentheses.) O*: bridging oxygen atoms**[SiO₄] tetrahedra**

Si–O distances		O–O distances		O–Si–O angles
Si(1)–O(1)	1.54(2)	O(1)–O(4)*	2.31(3)	93.1(1.3)
–O(2)	1.62(2)	O(3)*–O(4)*	2.56(3)	100.7(1.1)
–O(4)*	1.65(2)	O(1)–O(2)	2.63(2)	112.5(1.0)
–O(3)*	1.68(2)	O(2)–O(3)*	2.66(3)	107.0(1.4)
mean	1.623	O(1)–O(3)*	2.83(3)	122.7(1.2)
		O(2)–O(4)*	2.85(4)	120.9(1.7)
		mean	2.640	mean 109.5
Si(2)–O(5)	1.55(2)	O(3)*–O(5)	2.46(8)	103.6(3.9)
–O(3)*	1.58(3)	O(3)*–O(6)*	2.50(4)	101.3(1.7)
–O(4)*	1.64(2)	O(3)*–O(4)*	2.51(3)	101.9(1.2)
–O(6)*	1.65(1)	O(4)*–O(6)*	2.65(3)	107.4(1.2)
mean	1.605	O(5)–O(6)*	2.70(2)	115.4(1.0)
		O(4)*–O(5)	2.81(4)	123.7(2.8)
		mean	2.605	mean 108.9
Si(3)–O(7)	1.57(3)	O(6)*–O(8)*	2.54(4)	104.3(1.7)
–O(6)*	1.59(2)	O(8)*–O(8)*	2.56(3)	101.7(1.1)
–O(8)*	1.63(2)	O(6)*–O(7)	2.57(2)	109.1(1.3)
–O(9)*	1.66(2)	O(7)–O(8)*	2.63(9)	110.8(4.4)
mean	1.613	O(6)*–O(9)*	2.67(3)	110.3(1.2)
		O(7)–O(9)*	2.79(4)	119.5(3.1)
		mean	2.627	mean 109.3
Si(4)–O(10)	1.60(3)	O(8)*–O(9)*	2.55(3)	104.5(1.2)
–O(9)*	1.61(2)	O(8)*–O(11)*	2.57(3)	105.6(1.4)
–O(11)*	1.61(1)	O(9)*–O(11)*	2.58(4)	106.8(2.1)
–O(8)*	1.62(2)	O(9)*–O(10)	2.65(5)	111.9(2.1)
mean	1.610	O(10)–O(11)*	2.65(2)	111.4(1.2)
		O(8)*–O(10)	2.73(3)	116.0(1.8)
		mean	2.622	mean 109.4
Si–O–Si angles				
Si(1)–O(4)*–Si(2)	134.3(1.5)			
Si(1)–O(3)*–Si(2)	130.0(1.3)			
Si(2)–O(6)*–Si(3)	140.2(1.2)			
Si(3)–O(8)*–Si(4)	136.1(1.5)			
Si(3)–O(9)*–Si(4)	130.3(1.4)			
Si(4)–O(11)*–Si(4)	172.9(4.1)			
mean	140.6			

Table 4 (Continued)

[BaO ₈] polyhedra					
Si–O distances		O–O distances		O–Si–O angles	
Ba(1)–O(1)	2.69(3)	Ba(2)–O(5)	2.65(2)	Ba(3)–O(7)	2.78(10)
–O(1)	2.76(2)	–O(10)	2.66(5)	–O(7)	2.78(10)
–O(2)	2.76(2)	–O(6)*	2.79(2)	–O(10)	2.80(2)
–O(1)	2.84(3)	–O(2)	2.87(4)	–O(10)	2.80(2)
–O(4)*	2.85(2)	–O(2)	2.89(4)	–O(7)	2.86(10)
–O(5)	2.90(9)	–O(9)*	2.91(2)	–O(7)	2.86(10)
–O(3)*	2.97(2)	–O(7)	2.93(2)	–O(8)*	3.27(2)
–O(5)	2.99(9)	–O(10)	3.09(5)	–O(9)*	3.27(2)
mean	2.85	mean	2.85	mean	2.93
All other		All other		All other	
Ba(1)–O	> 3.59	Ba(2)–O	> 3.69	Ba(3)–O	> 3.47

Table 5. Interatomic distances (in Å) and bond angles (in °) in Ba₆[Si₁₀O₂₆], Standard deviations in parentheses.) O* : bridging oxygen atoms

[SiO ₄] tetrahedra					
Si–O distances		O–O distances		O–Si–O angles	
Si(1)–O(1)	1.61(2)	O(3)*–O(4)*	2.53(3)		98.8(0.9)
–O(2)	1.64(2)	O(1)–O(3)*	2.59(3)		104.0(1.0)
–O(3)*	1.67(2)	O(1)–O(4)*	2.72(2)		111.7(1.0)
–O(4)*	1.67(2)	O(1)–O(2)	2.74(2)		114.7(0.9)
mean	1.648	O(2)–O(4)*	2.75(3)		112.4(1.0)
		O(2)–O(3)*	2.77(3)		114.0(1.1)
		mean	2.683	mean	109.3
Si(2)–O(5)	1.58(2)	O(3)*–O(4)*	2.52(3)		102.5(0.9)
–O(4)*	1.60(2)	O(4)*–O(5)	2.62(3)		110.6(1.2)
–O(3)*	1.63(2)	O(3)*–O(6)*	2.64(2)		105.7(1.0)
–O(6)*	1.68(2)	O(4)*–O(6)*	2.67(3)		108.9(1.1)
mean	1.623	O(5)–O(6)*	2.70(3)		111.7(0.9)
		O(3)*–O(5)	2.74(2)		116.9(1.1)
		mean	2.648	mean	109.4
Si(3)–O(6)*	1.57(2)	O(6)*–O(8)*	2.53(3)		104.5(1.1)
–O(7)	1.58(2)	O(6)*–O(7)	2.54(3)		107.8(1.0)
–O(8)*	1.63(2)	O(8)*–O(9)*	2.59(3)		103.1(0.9)
–O(9)*	1.68(2)	O(6)*–O(9)*	2.65(2)		108.9(0.9)
mean	1.615	O(7)–O(8)*	2.71(3)		115.7(1.2)
		O(7)–O(9)*	2.77(3)		116.1(1.0)
		mean	2.632	mean	109.4
Si(4)–O(10)	1.55(2)	O(8)*–O(9)*	2.52(3)		102.7(0.9)
–O(9)*	1.59(2)	O(9)*–O(10)	2.58(3)		110.3(1.1)
–O(8)*	1.64(2)	O(9)*–O(11)*	2.58(3)		105.7(1.0)
–O(11)*	1.65(2)	O(8)*–O(11)*	2.60(3)		104.5(1.0)
mean	1.608	O(10)–O(11)*	2.71(3)		115.5(1.0)
		O(8)*–O(10)	2.72(3)		116.8(1.1)
		mean	2.618	mean	109.3

Table 5 (Continued)

[SiO ₄] tetrahedra					
Si—O distances		O—O distances		O—Si—O angles	
Si(5)—O(12)	1.58(2)	O(11)*—O(13)*	2.53(3)		105.4(1.0)
—O(13)*	1.58(2)	O(13)*—O(13)*	2.56(3)		104.1(1.0)
—O(11)*	1.60(2)	O(11)*—O(12)	2.58(3)		108.5(0.9)
—O(13)*	1.66(2)	O(12)—O(13)*	2.62(3)		111.6(1.1)
mean	1.605	O(11)*—O(13)*	2.66(3)		109.1(1.0)
		O(12)—O(13)*	2.77(3)		117.4(1.1)
		mean	2.620	mean	109.4
Si—O—Si angles					
Si(1)—O(3)*—Si(2)	129.1(1.2)				
Si(1)—O(4)*—Si(2)	132.8(1.3)				
Si(2)—O(6)*—Si(3)	139.6(1.1)				
Si(3)—O(8)*—Si(4)	132.9(1.2)				
Si(3)—O(9)*—Si(4)	129.8(1.1)				
Si(4)—O(11)*—Si(5)	153.1(1.2)				
Si(5)—O(13)*—Si(5)	136.8(1.2)				
mean	136.3				
[BaO ₈] polyhedra					
Ba(1)—O(1)	2.70(2)	Ba(2)—O(5)	2.69(2)	Ba(3)—O(12)	2.75(2)
—O(4)*	2.73(2)	—O(6)*	2.76(2)	—O(10)	2.75(2)
—O(1)	2.75(2)	—O(10)	2.77(2)	—O(7)	2.82(2)
—O(5)	2.80(2)	—O(2)	2.80(2)	—O(7)	2.85(2)
—O(1)	2.80(2)	—O(9)*	2.83(2)	—O(12)	2.93(2)
—O(2)	2.82(2)	—O(2)	2.91(2)	—O(12)	2.93(2)
—O(3)*	2.90(2)	—O(7)	2.95(2)	—O(11)*	2.97(2)
—O(5)	3.14(2)	—O(10)	3.22(2)	—O(13)*	3.02(2)
mean	2.83	mean	2.87	mean	2.88
All other		All other		All other	
Ba(1)—O	> 3.54	Ba(2)—O	> 3.82	Ba(3)—O	> 3.38

Description of the structures

In all three phases studied [SiO₄] tetrahedra are corner-linked to form *zweier* single chains with identity periods of approximately 4.7 Å. Three, four and five such single chains, respectively, are linked to a multiple chain, adjacent single chains being linked via every second tetrahedron. Henceforth, the single chains that comprise the multiple chains will be called *subchains*.

Ba₄[Si₆O₁₆]

The structure of this phase is shown in Figure 1². Triple chains running parallel [010] have 2₁ symmetry. Since the bridging oxygen atoms, O*, within

² For a more convenient comparison of the structures some of the projections were not drawn with the conventional orientations

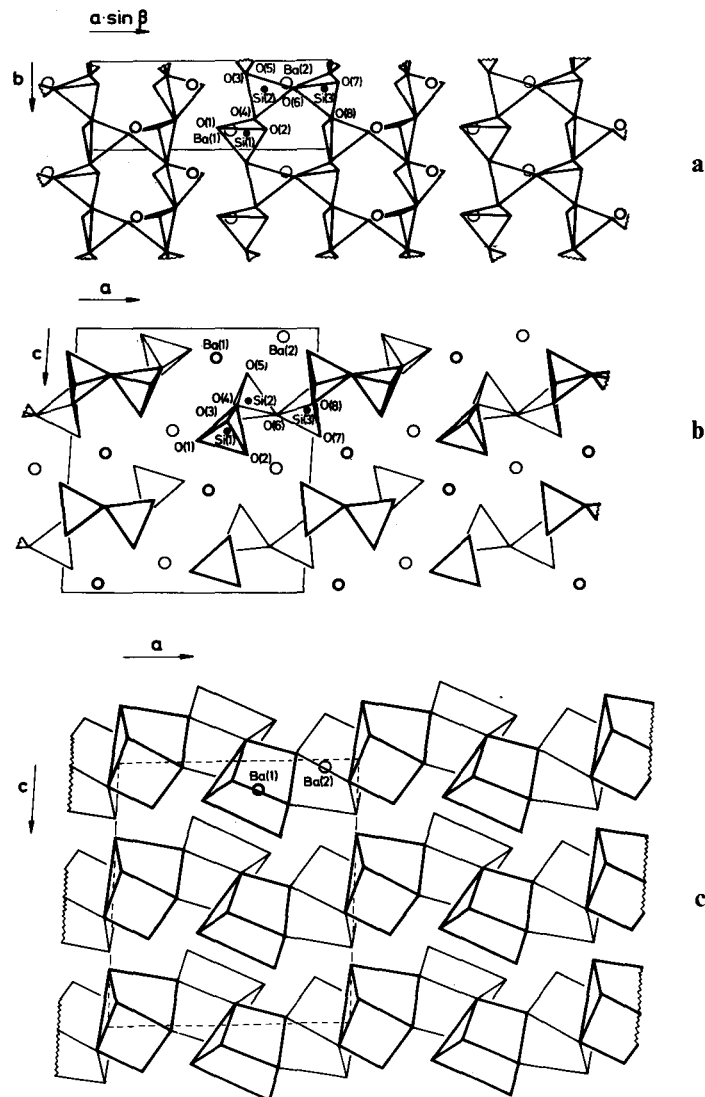


Fig. 1. $Ba_4[Si_6O_{16}]$; a) silicate chains within half the unit cell projected parallel $[001]$; b) silicate chains projected parallel $[010]$; c) corrugated layers of barium-oxygen polyhedra projected parallel $[010]$

a subchain do not lie on a straight line each tetrahedron within a subchain points to the same direction, either $[010]$ or $[0\bar{1}0]$. In $Ba_4[Si_6O_{16}]$ the tetrahedra of all three subchains forming one triple chain point to the same direction. Between adjacent triple chains there are twofold screw axes and

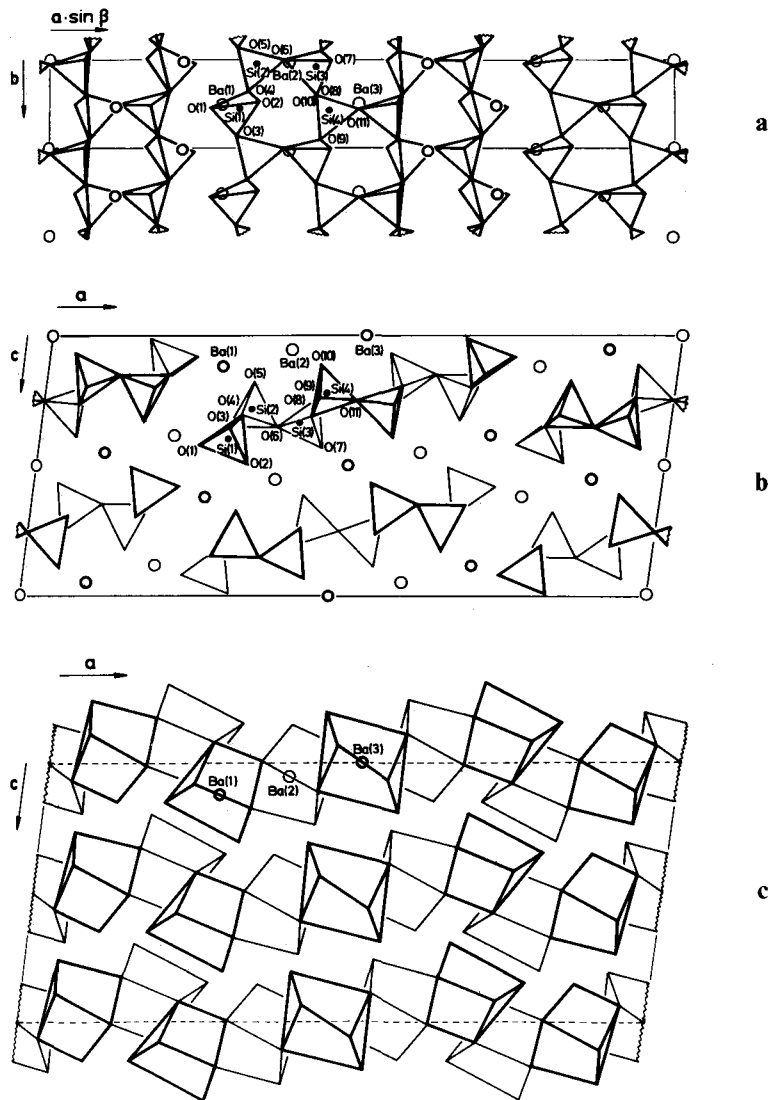


Fig. 2. $Ba_5[Si_8O_{21}]$; a) silicate chains within half the unit cell projected parallel $[001]$; b) silicate chains projected parallel $[0\bar{1}0]$; c) corrugated layers of barium-oxygen polyhedra projected parallel $[0\bar{1}0]$

inversion centres, so that half the multiple chains point parallel, the other half antiparallel to $[010]$.

This is in contradiction to the results derived by Filipenko et al. (1971) who rejected the symmetry $P2_1/c$ in favour of $P2_1$ because of what they call

crystal chemical reasons. They describe triple chains that have no symmetry and in which two subchains point parallel and the third antiparallel to [010] and vice versa. Because of the clear result of our statistical test on the existence of inversion centres, our better reliability index $R = 0.046$ compared with their $R = 0.08$, and of the fact that the distortions of the $[\text{SiO}_4]$ tetrahedra in our structure are within the range found in more accurately determined silicate structures, we believe that our structure is more accurate than that described by Filipenko et al. (1971).

Each of the two non-equivalent barium ions is coordinated by eight oxygen ions with bond distances between 2.64 \AA and 3.09 \AA (Fig. 1c and Table 3). The $[\text{BaO}_8]$ polyhedra may either be described as distorted cubes or better as distorted octahedra in which two nonadjacent vertices are split into two edges forming what may be called a bisplit octahedron. The polyhedron around Ba(1) is more distorted than that around Ba(2). There are columns of edge sharing $[\text{BaO}_8]$ polyhedra running parallel to [010]. Four such columns are linked to a band by sharing edges. Each band of polyhedra links two $[\text{Si}_6\text{O}_{16}]$ triple chains together. Adjacent polyhedral bands share edges to form corrugated layers parallel (001) (Fig. 1c).

$\text{Ba}_5[\text{Si}_8\text{O}_{21}]$

The quadruple chains of this phase have twofold rotation symmetry (Fig. 2). As in $\text{Ba}_4[\text{Si}_6\text{O}_{16}]$ the tetrahedra of all four subchains of a quadruple chain point to the same direction. Between adjacent quadruple chains there are inversion centres as well as twofold screw axes. There are three crystallographically non-equivalent $[\text{BaO}_8]$ polyhedra of which $[\text{Ba}(2)\text{O}_8]$ is the least distorted and $[\text{Ba}(3)\text{O}_8]$ is centrosymmetric. Five columns of edge sharing $[\text{BaO}_8]$ polyhedra at a time form a band running parallel [010] (Fig. 3), adjacent bands are linked via common edges to corrugated layers parallel (001) in the same way as the narrower bands in $\text{Ba}_4[\text{Si}_6\text{O}_{16}]$ (Fig. 2c). Interatomic distances and angles are given in Table 4.

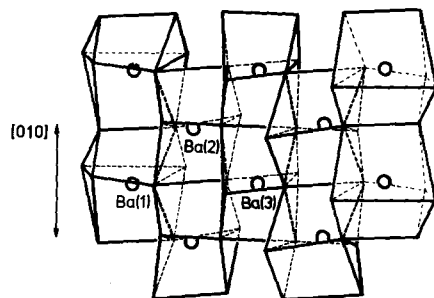


Fig. 3. Band of $[\text{BaO}_8]$ polyhedra in $\text{Ba}_5[\text{Si}_8\text{O}_{21}]$

$Ba_6[Si_{10}O_{26}]$

The quintuple chains of this phase have twofold screw symmetry (Fig. 4) like the triple chains in $Ba_4[Si_6O_{16}]$. In contrast to the multiple chains in

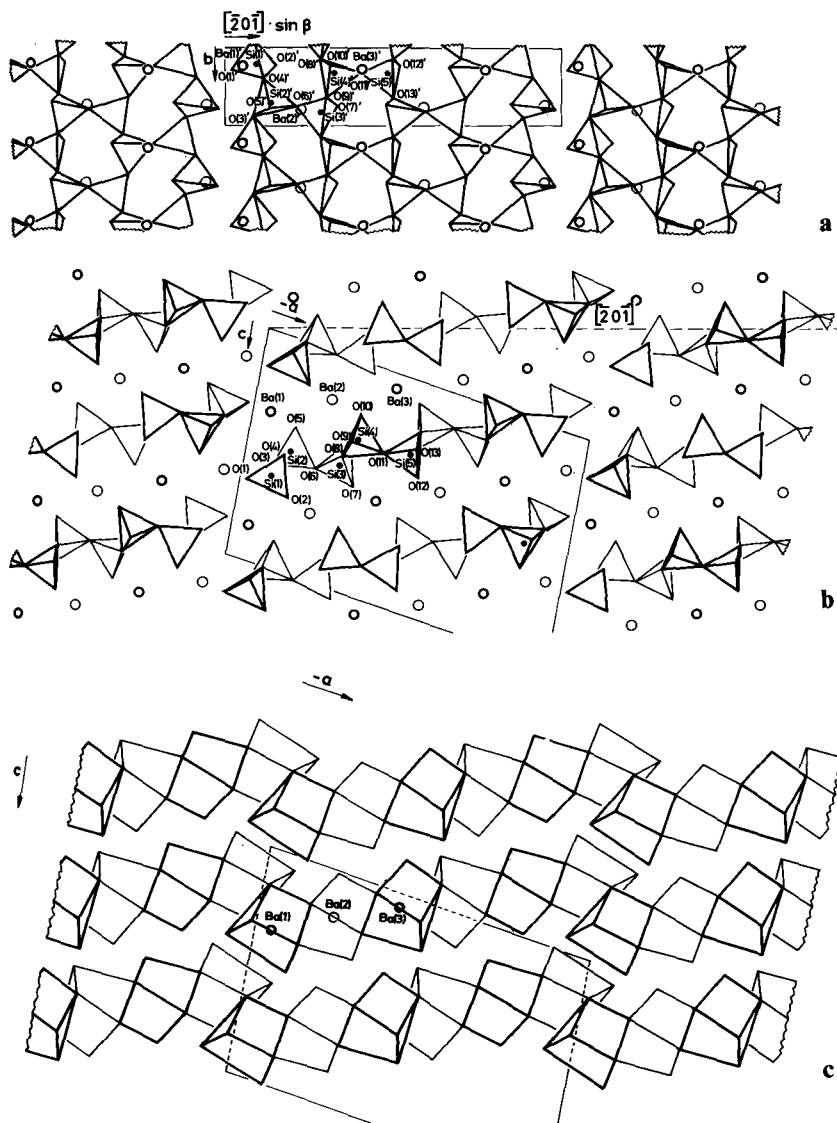


Fig. 4. $Ba_6[Si_{10}O_{26}]$: a) silicate chains within half the unit cell projected parallel $[00\bar{1}]$; b) silicate chains projected parallel $[010]$; c) corrugated layers of barium-oxygen polyhedra projected parallel $[010]$

