

Refinement of Tribarium Silicate

BY EKKEHART TILLMANN

Institut für Geowissenschaften, Postfach 3980, D-6500 Mainz, Federal Republic of Germany

AND HANS-PETER GROSSE

Dr C. Otto GmbH u. Comp., Postfach 9, D-4630 Bochum, Federal Republic of Germany

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Abstract. Ba_3OSiO_4 , tetragonal, $I4/mcm$ with $a = 7.3023(6)$, $c = 11.2178(9)$ Å, $Z = 4$, $D_x = 5.78$ g cm^{-3} . The crystal structure was refined to $R = 0.044$ for 526 reflections. Ba_3OSiO_4 is isostructural with $\text{Cs}_3\text{ClCoCl}_4$. The SiO_4 tetrahedra are slightly distorted with O–Si–O angles of 110.6 and 107.2° respectively and $d(\text{Si–O}) = 1.639$ Å. The two crystallographically different Ba atoms are coordinated by ten [Ba(1)] and eight O atoms [Ba(2)] with mean Ba–O distances of 2.988 and 2.81 Å respectively.

Introduction. Ba_3OSiO_4 has been reported to be isostructural with either Sr_3OSiO_4 or $\text{Cs}_3\text{ClCoCl}_4$ (Mansmann, 1965). Although the latter two compounds have similar structures there are distinct differences since they crystallize in different space groups and the coordinations of the large cations are different. Because of the difficulty in growing single crystals of Ba_3OSiO_4 , earlier X-ray investigations were based on powder data and a detailed account of the crystal structure has not yet been reported. A single crystal of almost spherical shape with a diameter of about 0.16 mm, grown by solid-state reaction as described by Grosse (1976), was used to measure the cell parameters and intensities. The cell constants were refined by a least-squares fit to the angular settings of 30 reflections with $\theta > 20^\circ$ measured on an automatic four-circle diffractometer (Mo $K\alpha_1$, $\lambda = 0.70926$ Å). The systematic absences (hkl with $h + k + l$ odd and $0kl$ with l odd) indicate space groups $I4cm$, $I4c2$ and $I4/mcm$. The results of the refinement indicate space group $I4/mcm$.

The intensities of 3741 reflections with $\theta \leq 35^\circ$ were collected on the diffractometer with monochromatic Mo $K\alpha$ radiation (graphite monochromator) and the ω - 2θ step-scan mode with a scan range of $\Delta\omega = (0.5 + 0.5 \tan \theta)$. The diffracted-beam aperture was vertically constant (4 mm) and horizontally determined by $(4 + 2 \tan \theta)$ mm. The scanning speed was adjusted to obtain 5000 counts for each reflection with a maximum counting time of 180 s. The background was measured for one-quarter of the scan time on both sides of the peak.

After correction for absorption [$\mu(\text{Mo } K\alpha) = 202.4$ cm^{-1} , transmission factors between 0.12 and 0.15] the reduction and averaging of the intensity data resulted in 526 unique structure factors, 79 of which were considered to be of zero intensity ($I < 2\sigma_I$).

The structure was refined by full-matrix least-squares calculations, starting from the positional parameters of $\text{Cs}_3\text{ClCoCl}_4$ given by Figgis, Gerloch & Mason (1964). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1968). The observed structure factors were weighted according to $w = 1/\sigma^2(F)$. The computer programs used in the

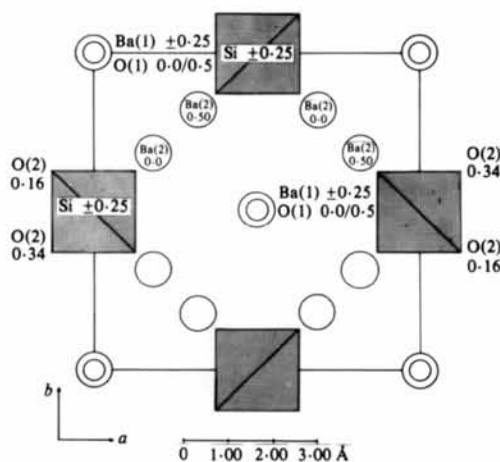


Fig. 1. Ba_3OSiO_4 , projection of the crystal structure along $[001]$. Large circles are Ba atoms; the heights of the atoms are given as fractional coordinates.

Table 1. Ba_3OSiO_4 , fractional atomic coordinates ($\times 10^4$) with estimated standard deviations

	x	y	z
Ba(1)	0	0	$\frac{1}{2}$
Ba(2)	1832 (1)	6832	0
Si	0	$\frac{1}{2}$	$\frac{1}{2}$
O(1)	0	0	0
O(2)	1278 (6)	6278	3367 (5)

course of the work are the same as those given by Tillmanns & Gebert (1973).

After an extinction correction (Zachariasen, 1963; $C = 3.5 \times 10^{-5}$) the final weighted residual $R_2 = [\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2}$ was 0.039; the corresponding unweighted R_1 was 0.028 for the observed reflections and 0.044 including the 79 unobserved reflections with $F_o = 0$. The greatest shift in the last cycle of refinement was 0.02σ for β_{12} of O(2), the largest maxima or minima in the final difference synthesis were $\pm 3 e \text{ \AA}^{-3}$ around the Ba atoms. The refined positional parameters are given in Table 1.*

Discussion. In his work on the crystal structures of Ba_3MO_5 compounds with $M = Ti, V, Cr, Mn, Fe, Co, Si$ and Ge Mansmann (1965) could not decide whether Ba_3OSiO_4 was isostructural with $Cs_3ClCoCl_4$ (Figgis, Gerloch & Mason, 1964) or with Sr_3OSiO_4 (Glasser & Glasser, 1965). The major difference between the two structures is the relative position of the SiO_4 tetrahedra which are superimposed in the c direction at a distance of $\frac{1}{2}c$. In Ba_3OSiO_4 the tetrahedra are strictly parallel with their upper and lower edges parallel to the face diagonal of the (001) plane (Fig. 1); in Sr_3OSiO_4 they are rotated with respect to each other through an angle of 33° , which leads to the lower symmetry of space group $P4/ncc$ instead of $I4/mcm$. The different position of the tetrahedral O(2) atom also causes a different

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33074 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

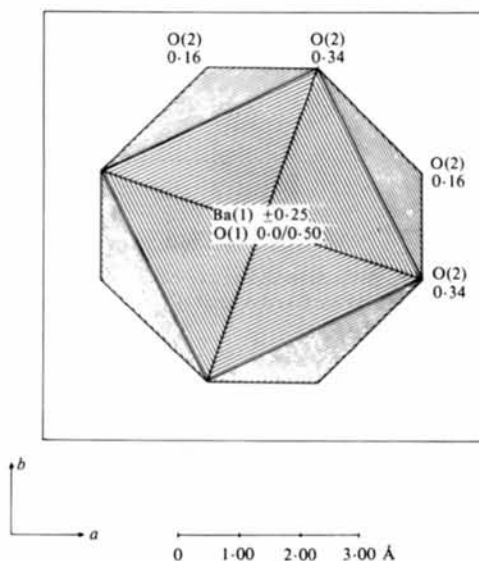


Fig. 2. Coordination polyhedron around Ba(1).

coordination of the large Ba and Sr cations. While in Sr_3OSiO_4 Sr(1) and Sr(2) have distorted octahedral coordinations with four and two O atoms, respectively, at distances greater by 20% than the average of the six shorter ones, the coordination of Ba atoms in Ba_3OSiO_4 is clearly tenfold for Ba(1) and eightfold for Ba(2).

The Ba(1)O₁₀ coordination polyhedron is a quadratic antiprism with two additional O atoms above and below the base faces (Fig. 2). The irregular eight-coordination around Ba(2) is shown in Fig. 3.

Table 2 lists interatomic distances and angles. The SiO_4 tetrahedron is only slightly distorted with four Si—O distances of 1.639 Å and O—Si—O angles of 110.6 and 107.2°. All six edges are shared with the coordination polyhedra around Ba. The range of Ba—O distances is rather low with 2.805–3.034 Å for the Ba(1)O₁₀ polyhedron (mean value: 2.988 Å) and 2.673–2.945 Å for Ba(2) (mean value: 2.810 Å).

The average Ba—O distance of 2.988 Å in the Ba(1)O₁₀ coordination polyhedron is large. Fischer (1972) gives a much smaller average distance of 2.87 Å for compounds containing Ba in 10-coordination and even for 11 or 12-coordinated Ba; for example, in a number of barium titanates (Tillmanns, 1976) smaller average Ba—O distances have been found (2.88–2.97 Å).

The size of the coordination polyhedron seems to be responsible for the difference in the crystal structures of Ba_3OSiO_4 and Sr_3OSiO_4 . The rotation of SiO_4 tetra-

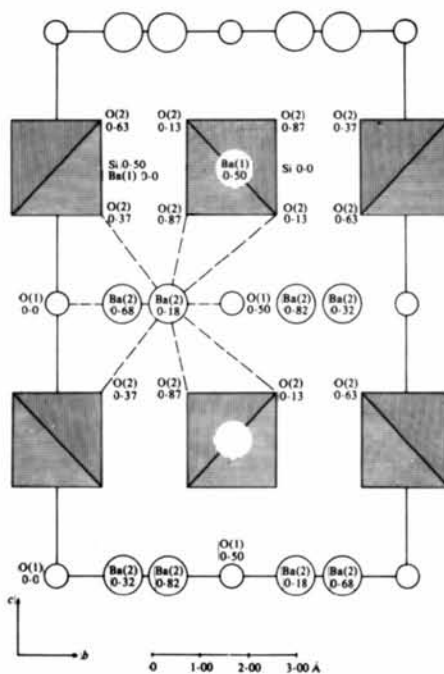


Fig. 3. Ba_3OSiO_4 , projection of the crystal structure along [100]. Large circles are Ba atoms; the heights of the atoms are given as fractional coordinates.

hedra with respect to each other in Sr_3OSiO_4 causes a lower coordination number of six for Sr(1) with an average Sr—O distance of 2.600 Å (Glasser & Glasser, 1965). Without rotation of the tetrahedra, Sr(1) would be ten-coordinated with a large average distance of 2.84 Å, an arrangement which is electrostatically less

favourable. A similar situation has been found in the crystal structure of Ba_2SiO_4 (Grosse & Tillmanns, 1974). Average Ba—O distances are 2.983 Å for the $\text{Ba}(1)\text{O}_{10}$ polyhedron and 2.824 Å for the nine-coordinated Ba(2) atom. A detailed account of the crystal structure of Sr_2SiO_4 has not been given so far, but Pieper, Eysel & Hahn (1972) report that Sr_2SiO_4 has two crystalline modifications: α' - Sr_2SiO_4 above approximately 85°C is probably isostructural with Ba_2SiO_4 , β - Sr_2SiO_4 below 85°C is isostructural with β - Ca_2SiO_4 . The main difference between the two structures is that in β - Ca_2SiO_4 (Cruckshank, 1964) SiO_4 tetrahedra are rotated so that the Ca atom which corresponds to Ba(1) in Ba_2SiO_4 is only six-coordinated with the other four O atoms at distances greater by 20% than the average of the six short Ba—O bonds.

Table 2. Ba_3OSiO_4 , interatomic distances (Å) and angles (°)

Standard deviations are approximately 0.004 Å for Ba—O and Si—O distances and 0.006 Å for O—O distances. Bond angles have a standard deviation of 0.2°.

Coordination around Ba(1)			
Ba(1)—O(1)		2.805 (2×)	
—O(2)		3.034 (8×)	
O(1)—O(2)	108.7	4.746 (8×)	
O(1)—O(2)	71.3	3.408 (8×)	
O(2)—O(2)	84.1	4.064 (8×)	
O(2)—O(2)	52.8	2.696 (4×)	
O(2)—O(2)	144.2	5.773 (4×)	
O(2)—O(2)	63.4	3.187 (4×)	
O(2)—O(2)	130.8	5.518 (4×)	
O(2)—O(2)	142.6	5.747 (4×)	
O(1)—O(1)	180.0	5.609	
Coordination around Ba(2)			
Ba(2)—O(1)		2.673 (2×)	
—O(2)		2.677 (2×)	
—O(2)		2.945 (4×)	
O(1)—O(1)	150.1	5.164	
O(1)—O(2)	79.1	3.408 (4×)	
O(1)—O(2)	74.5	3.408 (4×)	
O(1)—O(2)	126.8	5.024 (4×)	
O(2)—O(2)	86.4	3.664	
O(2)—O(2)	92.5	4.064 (4×)	
O(2)—O(2)	153.4	5.472 (4×)	
O(2)—O(2)	100.1	4.516 (2×)	
O(2)—O(2)	53.2	2.640 (2×)	
O(2)—O(2)	76.9	3.664 (2×)	
Coordination around Si			
Si—O(2)		1.639 (4×)	
O(2)—O(2)	110.6	2.696 (4×)	
O(2)—O(2)	107.2	2.640 (2×)	

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