Zeitschrift für Kristallographie 169, 219–225 (1984)

The crystal structure of $Ba_2[SiO_2(OH)_2]_2$

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Received: July 9, 1984

Barium / Silicate / Structure

Abstract. The crystal structure of $Ba_2[SiO_2(OH)_2]_2$, (triclinic, $a = 7.0793(4)$ Å, $b = 7.3585(5)$ Å, $c = 7.5814(5)$ Å, $\alpha = 90.357(6)°$, $\beta = 88.792(6)°$, $\gamma = 91.793(6)°$, $P\bar{1}$, $Z = 2$, $V = 394.7$ Å^3, $D_c = 3.90$ g cm^{-3}) was solved by Patterson synthesis and subsequent Fourier methods, and refined to $R = 0.021$ for 4880 reflexions.

The structure consists of isolated $[SiO_2(OH)_2]^{2-}$ tetrahedra connected by hydrogen bonds. The barium atoms are coordinated by nine oxygens in distorted capped square antiprisms.

Introduction

During the investigation of the sodium-barium-aluminium-silicate system some hydrothermal crystallizations yielded crystals of analcime, harmotome and up to 2 mm large crystals of a phase which could be shown to be identical with the phases described as zeolite Ba – T (Barrer and Mainwaring, 1972) and $BaO \cdot SiO_2 \cdot H_2O$ (Krüger and Wieker, 1965). The first lines of the powder photographs are listed in a table, which has been deposited. A semi-quantitative X-ray fluorescence analysis of the material showed different amounts of aluminium in the crystals with the ratio Si : Al varying from 2 : 1 to almost aluminium-free crystals. A difference in the ratio between different parts of the crystals was also observed, which indicates that the composition can vary within wide ranges. In the structure refinement all the tetrahedral sites are treated as silicons, the correctness of which is also indicated by the estimated interatomic distances.

Experimental

Single crystals of the title compound were prepared using the method described by Fälth (1981) at 150 °C. The reactants were a sodium-

Table 1. Experimental details

Cell data	$a = 7.0793(4)$ Å $b = 7.3585(5)$ Å $c = 7.5814(5)$ Å $\alpha = 90.357(6)°$ $\beta = 88.792(6)°$ $\gamma = 91.793(6)°$ $Z = 2$
Space group	$P\bar{1}$
Calculated density	$D_c = 3.90$ g cm^{-3}
Radiation; wave length (Å)	Mo$K\alpha$; 0.71069
θ interval (°)	1.5 – 40
$\omega - 2\theta$ scan width $\Delta 2\theta$	2.4° + $\alpha_1\alpha_2$-splitting
Scan rate	1.0 – 29.3°/min
Total background time	equal to scan time
Linear absorption coefficient, μ	10.5 mm^{-1}
Range of transmission factors	0.24 – 0.72
Number of reflexions measured[a]	5193
Number of reflexions with zero weight	313 $[I < 3\sigma_c(I)]$
Number of reflexions used in the final refinement, m	4880
Number of parameters refined, n	110
$R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	0.021
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.028
$S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(m-n)]^{1/2}$	0.70
$g(\times 10^{-4})$ extinction	0.11

[a] one set of independent reflexions was used

barium-aluminosilicate glass, NaOH and $Ba(OH)_2$ solution. The cell dimensions, shown in Table 1, were refined by least-squares methods from 55 singly indexed lines of a powder pattern obtained in a Guinier-Hägg focusing camera with Cu$K\alpha_1$ radiation. A platy triangular crystal ($0.250 \times 0.390 \times 0.030$ mm^3), selected using the Weissenberg technique, was mounted on a Nicolet $P3$m four-circle diffractometer and the unit cell was confirmed by the least-squares refinement of 15 accurately measured θ-values.

Table 1 gives information on the data collection, reduction of the intensities and subsequent refinement. During the data collection no systematic variation was observed in three standard reflexions which were checked every 50 reflexions. I and $\sigma_c(I)$ (based on counting statistics) were corrected for Lorentz and polarization effects. The positions of the two barium atoms were determined from the three-dimensional Patterson function and repeated difference syntheses, and full-matrix least-squares refinement minimizing $\Sigma w(|F_o| - |F_c|)^2$ with weights $w^{-1} = \sigma_c^2(|F_o|) + (0.02|F_o|)^2 + 1.0$ revealed the positions of the remaining atoms. The hydrogen atoms were included in the final least-squares refinement with fixed positional and thermal parameters.

Table 2. Final positional parameters and isotropic B values. Standard deviations in parentheses

	x	y	z	$B[Å^2]$
Ba(1)	0.06533(2)	0.18868(1)	0.20049(1)	0.81(0)
Ba(2)	0.37159(2)	0.26041(1)	0.70884(1)	0.85(0)
Si(1)	0.57406(8)	0.24196(7)	0.20747(7)	0.73(1)
Si(2)	0.10909(8)	0.72959(7)	0.28938(7)	0.72(1)
O(1)	0.44652(23)	0.15693(22)	0.04876(29)	1.07(2)
O(2)	0.71695(26)	0.40746(22)	0.12922(21)	1.19(3)
O(3)	0.43538(25)	0.33975(23)	0.35485(21)	1.19(3)
O(4)	0.70000(22)	0.09608(20)	0.30187(20)	1.00(2)
O(5)	0.25552(25)	0.89315(24)	0.36500(21)	1.24(3)
O(6)	0.23761(26)	0.56643(23)	0.21182(22)	1.29(3)
O(7)	−0.02691(23)	0.65992(21)	0.45398(20)	1.04(2)
O(8)	−0.01461(22)	0.82120(21)	0.14156(19)	0.95(2)
H(11)	0.4570	0.0831	0.0032	5.00
H(26)	0.7348	0.4031	0.0155	5.00
H(36)	0.3849	0.4293	0.2927	5.00
H(63)	0.2788	0.4839	0.2831	5.00
H(54)	0.2663	0.8845	0.4757	5.00
H(77)	0.0000	0.5819	0.4881	5.00

They were taken from peaks in a Fourier map having the electron density of about 1 $e/Å^3$.

Atomic scattering factors for neutral atoms (Doyle and Turner, 1968) were used. All factors except those for hydrogen were corrected for anomalous dispersion (Cromer and Liberman, 1970). Anisotropic temperature factors for the non-hydrogen atoms, correction for absorption by numerical integration and isotropic extinction (Zachariasen, 1968) gave the final values $R = 0.021$ and $R_w = 0.028$. Final positions parameters are given in Table 2 and selected bond lengths and angles in Tables 3 and 4.[1]

Description of the structure

The structure of $Ba_2[SiO_2(OH)_2]_2$ projected along the c-axis is illustrated in Fig. 1. It consists of isolated $[SiO_2(OH)_2]^{2-}$ tetrahedra, which are held together by barium ions and by hydrogen bonds. The arrangement of the tetrahedra and the cations is similar to that found in $CaHPO_4$ (MacLennan and Beevers, 1955; Dickens et al., 1971). The smaller size of the PO_4 tetrahedra and the calcium atoms in $CaHPO_4$ causes the cell parameters to be less than in the title compound.

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[1] Additional material to this paper can be ordered referring to the no. CSD 51075, name(s) of the author(s) and citation of the paper at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG

Table 3. Selected bond distances (Å). Symmetry code: superscripts: none *x,y,z*; (i) $\bar{x},\bar{y},\bar{z}$

Si(1) tetrahedron		Si(2) tetrahedron	
Si(1)-O(4)	1.599(2)	Si(2)-O(8)	1.602(2)
Si(1)-O(1)	1.630(2)	Si(2)-O(6)	1.629(2)
Si(1)-O(3)	1.649(2)	Si(2)-O(7)	1.635(2)
Si(1)-O(2)	1.663(2)	Si(2)-O(5)	1.670(2)
O(1)-O(2)	2.693(2)	O(5)-O(6)	2.664(2)
O(1)-O(3)	2.676(2)	O(5)-O(7)	2.672(2)
O(1)-O(4)	2.704(2)	O(5)-O(8)	2.621(2)
O(2)-O(3)	2.637(2)	O(6)-O(7)	2.696(2)
O(2)-O(4)	2.644(2)	O(6)-O(8)	2.692(2)
O(3)-O(4)	2.656(2)	O(7)-O(8)	2.654(2)

Ba(1) polyhedron		Ba(2) polyhedron	
Ba(1)-O(8^{i})	2.626(1)	Ba(2)-O(4^{i})	2.657(2)
Ba(1)-O(4)	2.749(2)	Ba(2)-O(1)	2.759(2)
Ba(1)-O(8)	2.781(2)	Ba(2)-O(3)	2.775(2)
Ba(1)-O(7^{i})	2.851(2)	Ba(2)-O(8^{i})	2.798(2)
Ba(1)-O(5)	2.896(2)	Ba(2)-O(2^{i})	2.811(2)
Ba(1)-O(1)	2.927(2)	Ba(2)-O(7^{i})	2.837(2)
Ba(1)-O(6)	3.002(2)	Ba(2)-O(5^{i})	2.945(2)
Ba(1)-O(2)	3.047(2)	Ba(2)-O(6^{i})	3.079(2)
Ba(1)-O(3)	3.066(2)	Ba(2)-O(3^{i})	3.240(2)
Ba(1)-O(5^{i})	4.000(2)	Ba(2)-O(5)	3.826(2)

Distances oxygen-oxygen outside the tetrahedra (< 3.0 Å)

O(1)-O(1^{i})	2.553(3)
O(2)-O(6^{i})	2.606(2)
O(3)-O(6)	2.480(2)
O(4^{i})-O(5)	2.552(2)
O(7)-O(7^{i})	2.502(3)

Distances involving the hydrogen atoms

O(1)-H(11)	0.647	O(3)-H(63)	1.660
O(1^{i})-H(11)	1.949	O(6)-H(63)	0.876
O(2)-H(26)	0.869	O(4^{i})-H(54)	1.713
O(6^{i})-H(26)	1.745	O(5)-H(54)	0.847
O(3)-H(36)	0.899	O(7)-H(77)	0.666
O(6)-H(36)	1.607	O(7^{i})-H(77)	1.852

The two crystallographically different barium atoms are coordinated by nine oxygen atoms with mean Ba-O distances of 2.883 Å and 2.878 Å respectively. The Ba-O distances range from 2.626 Å to 3.240 Å and the coordination numbers are comparable to those found in other orthosilicates containing Ba atoms e.g. Ba_2SiO_4 (Grosse and Tillmanns, 1974), 2.640-3.174 Å, *CN* = 9, 10; Ba_3OSiO_4 (Tillmanns and Grosse, 1978),

Table 4. Selected bond angles (°)

Si(1) tetrahedron		Si(2) tetrahedron	
O(1) – Si(1) – O(2)	109.7(1)	O(5) – Si(2) – O(6)	107.7(1)
O(1) – Si(1) – O(3)	109.4(1)	O(5) – Si(2) – O(7)	107.9(1)
O(1) – Si(1) – O(4)	113.7(1)	O(5) – Si(2) – O(8)	106.4(1)
O(2) – Si(1) – O(3)	105.5(1)	O(6) – Si(2) – O(7)	111.4(1)
O(2) – Si(1) – O(4)	108.3(1)	O(6) – Si(2) – O(8)	112.9(1)
O(3) – Si(1) – O(4)	109.7(1)	O(7) – Si(2) – O(8)	110.2(1)

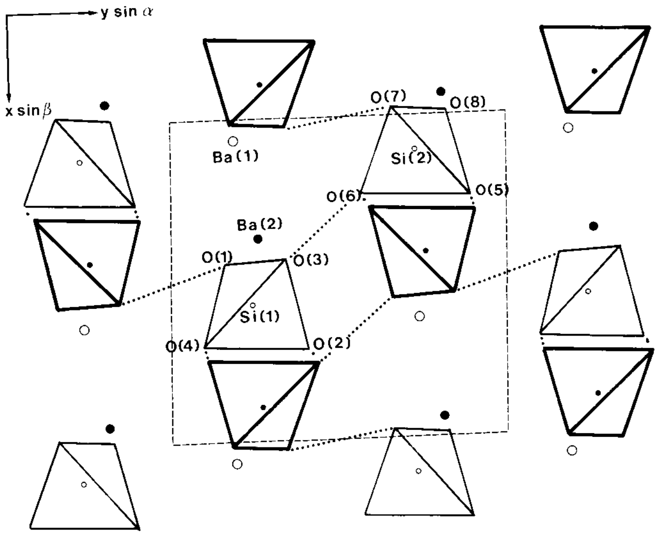

Fig. 1. The structure of $Ba_2[SiO_2(OH)_2]_2$ projected along the *c*-axis. Notice that the hydrogen bonds O(2) – O(6^i) are not on the same level as O(4) – O(5^i)

2.673 – 3.034 Å, *CN* = 8, 10 and $BaO \cdot SiO_2 \cdot 6H_2O$ (Höhne and Dornberger-Schiff, 1961), 2.83 – 3.0 Å, *CN* = 8, 10.

The BaO_9 coordination polyhedra may be described as distorted capped square antiprisms. Each Ba atom is linked to three Si-tetrahedra edges and to three Si-tetrahedra corners. Fig. 2 shows a stereo drawing of the $Ba(1)O_9$ polyhedron along the *c*-axis. O(1) – O(3) and O(2) – O(4) are edges in the Si(1)-tetrahedra and O(5) – O(8) is the edge in the Si(2)-tetrahedron. The three remaining oxygen atoms O(6), O(7) and O(8) are corners in three Si(2)-tetrahedra. The capping oxygen atom in the capped square antiprism is O(3).

A study of the bond lengths shows that a system of hydrogen bonds links the oxygen atoms. Table 2 lists those oxygen-oxygen distances, which

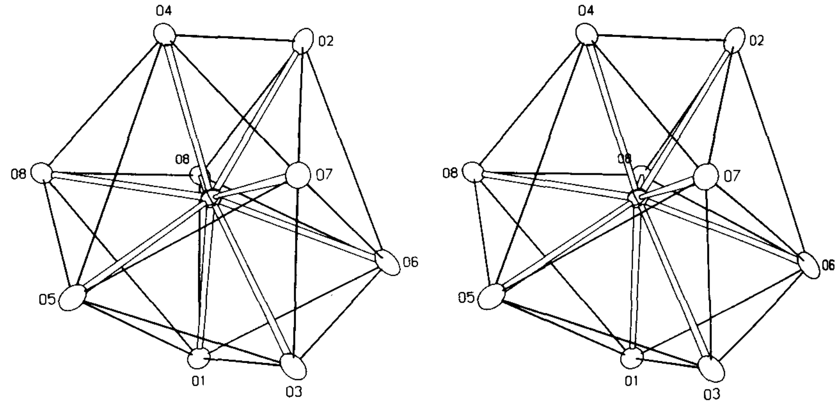

Fig. 2. A stereo drawing of the Ba(1) coordination. The *b*-axis points to the right and the *c*-axis out of the plane of the paper

represent hydrogen bonds. These are marked in Fig. 1 with dotted lines. O(8), which is not included in the list, has its shortest distance to O(4) at 3.12 Å. The hydrogen atoms link the "upper" oxygen of the tetrahedra to the "lower" oxygen of the neighbouring tetrahedra. In the [001] direction the Si(1) and Si(2) tetrahedra form "zig-zag" chains.

The short Si – O distances (Si(1) – O(4) and Si(2) – O(8)) and the longer Si – OH distances (Si(1) – O(2) and Si(2) – O(5)) are in good agreement with those found in a number of sodium silicate hydrates containing $[SiO_2(OH)_2]^{2-}$ and $[SiO_3(OH)]^{3-}$ tetrahedra e.g. $Na_2H_2SiO_4 \cdot 4H_2O$ (Jost and Hilmer, 1966), $Na_2H_2SiO_4 \cdot 5H_2O$ (Jamieson and Dent Glasser, 1967 and Williams and Dent Glasser, 1971), $Na_2H_2SiO_4 \cdot 8H_2O$ (Jamieson and Dent Glasser, 1966), $Na_2H_2SiO_4 \cdot 7H_2O$ (Dent Glasser and Jamieson, 1976), $Na_3HSiO_4 \cdot 5H_2O$ (Smolin et al., 1973) and $Na_3HSiO_4 \cdot 2H_2O$ (Schmid et al., 1979).

The hydrogen atoms H(11) and H(77) are placed near the centre of symmetry between the centrosymmetrically related atoms O(1), O(1^i) and O(7), O(7^i). The difference map showed two possible hydrogen positions (H(36) and H(63)) between the atoms O(3) and O(6). These hydrogen atoms fill only half of the two available sites. This probably explains the rather short Si – OH distances which are in the range of 1.629 – 1.649 Å.

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