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## Abstract

## Full Text

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## CRYSTALLOGRAPHY

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# CRYSTAL STRUCTURE OF SYNTHETIC BARIUM SILICATE

## $Ba_5[Si_4O_{12}](OH)_2$

This new barium silicate was obtained under hydrothermal conditions in the system BaO—$SiO_2$—$H_2O$ from a charge with the ratio $Ba(OH)_2 : SiO_2 = 7 : 1$ at 400–450° and 1500 atm. ([1]). The chemical composition (analysis by V. S. Bykova, Yu. S. Nesterova, and G. N. Arapova): $SiO_2$ 22.40%, BaO 74.62%, $H_2O$ 2.14%, $\Sigma = 99.06\%$, agrees sufficiently well with the formula $Ba_5[Si_4O_{12}](OH)_2$.

For the crystal-structure analysis, transparent colorless short-prismatic crystals of $Ba_5[Si_4O_{12}](OH)_2$ (Fig. 1) with optimal dimensions of 0.2–1.5 mm were used. At a specific gravity of 4.64 g/cm$^3$, the tetragonal cell with parameters refined on a DRON-1, $a = 7.745 \pm 6$, $c = 11.680 \pm 6$, contains $z = 2$ formula units $Ba_5[SiO_{12}](OH)_2$.

The diffraction symmetry group was determined from the $hk0$—$hk2$ and $h0l$ scans (KFOR X-ray goniometer, Mo radiation). Systematic extinctions in the reflections $h0l$ $(h + l = 2n + 1)$ and $hhl$ $(l = 2n + 1)$ led to two Fedorov groups, $P4_2/mnc$ and $P\bar{4}nc$.

The three-dimensional set of moduli of the structure amplitudes was obtained on a spherical sample of $Ba_5[Si_4O_{12}](OH)_2$ (mean diameter $0.224 \pm 0.005$ mm, deviation from sphericity 4%) in an automatic equi-inclination diffractometer DAR-UM ([2]), incorporating the DNEPR-1 control computer.

**Fig. 1.** External appearance of crystals of $Ba_5[Si_4O_{12}](OH)_2$

The following initial data were entered into the DAR-UM diffractometer: cell parameters, extinctions, sample dimensions, its mosaicity $M = 0.4°$, tube-focus projection 0.4 mm, characteristic-radiation wavelength Cu$K\alpha$, and absorption

Figure 2 and Figure 3

Figure 2: Figure 2 and Figure 3

multiplier for $\mu R = 12.2$ (from tables). In measurements with Cu$K\alpha$ radiation with a $\beta$-filter, a spectral interval equal to the resolution of the doublet, composed of 5 half-widths of the doublet components, was used; the number of measurement cycles was set equal to unity for all reflections; the scanning rate in $\omega$ was 8° per minute; the measurements covered 1/4 of the limiting sphere. The method for measuring the integrated intensity was $\omega$—$\omega/2\omega$, with control reflections every 30 min. ([3]).

At the diffractometer output, moduli of the structure amplitudes corrected for the $LP$ factors and absorption were obtained. Approximately 1200 reflections in 7 layer planes were recorded at an average rate of 56 reflections per hour. The mean error, determined from equivalent reflections within one layer, was 3.4%, and from reflections in different layers, 3.9%. After averaging over 4 equivalent reflections, the mean error for independent structure amplitudes, determined from the scatter of equivalent reflections, was 1.9%.

**Table 1**

**Coordinates of the basis atoms in the structure of** $Ba_5[Si_4O_{12}](OH)_2$

| Atoms | $x/a$ | $y/b$ | $z/c$ | Atoms | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|---|---|---|---|
| $Ba_1$ | 0.3409 | – | 0.250 | $O_1$ | 0.125 | 0.334 | 0.114 |
| $Ba_2$ | 0 | 0 | 0 | $O_2$ | 0.409 | 0.279 | 0 |
| Si | 0.114 | 0.275 | 0.500 | $O_3$(OH) | 0 | 0 | 0.250 |

The absence of a piezoelectric effect and the goniometric study of the crystals made it possible to regard holohedral symmetry as more probable. On the basis of the multiplicities of the positions in the Fedorov group $P4/mnc$, it was possible *a priori* to suppose that 10 Ba atoms and 8 Si atoms are combined into several particular point complexes. The positions of two crystallographically independent Ba atoms with multiplicities

**Fig. 2.** Plan of the structure. Large spheres are $Ba_1$, small ones are $Ba_2$

**Fig. 3.** Side projection of the structure. $A$—motif of linkage of $Ba_1$-15-hedra, spheres are $Ba_2$; $B$—$Ba_2$-12-hedra with $[Si_4O_{12}]$ rings, layer of spheres—$Ba_2$.

2 and 8 and Si atoms with multiplicity 8 were established from the three-dimensional Patterson function. Further determination of the structure was carried out by three-dimensional $F$-synthesis (two stages of approximation), with subsequent refinement of the parameters by the least-squares method. All calculations were performed at the Computing Center of Moscow University on an M-20, using programs by B. L. Tarnopolsky and V. I. Andrianov ([4]).

The final coordinates of the basis atoms of $Ba_5[Si_4O_{12}](OH)_2$ are given in Table 1. The accuracy of localization of the atoms is Ba ±0.0008 Å, Si ±0.006 Å, O ±0.01 Å. The discrepancy factor for 310 reflections different from zero up to $\max\sin\theta/\lambda = 0.63$, $R_{hkl} = 7.3\%$. The high value $\mu R = 12.2$ apparently led to a systematic error in introducing the absorption correction (the correction factors were obtained by extrapolation of a table ([5])), which affected the value of the averaged constant of isotropic thermal corrections ($B \sim 0.1$ Å$^2$).

The interatomic distances corresponding to the refined coordinates are given in Table 2 and agree well with the usual values in silicates. A sufficiently clear valence balance for atom $O_3$ distinguishes OH groups, which agrees with the IR spectrum.*

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**Table 2**

**Interatomic distances in the structure of** $Ba_5[Si_4O_{12}](OH)_2$ **(in angstroms)**

| Si tetrahedra | | $Ba_1$ polyhedra | | $Ba_2$ polyhedra | |
|---|---|---|---|---|---|
| Si $-O_1$ | 1.60 (2) | Ba $-O_1$ | 2.67 (2) | Ba $-O_1$ | 3.06 (8) |
| Si $-O_2$ | 1.64 | Ba $-O_1$ | 2.71 (2) | Ba $-O_3$ | 2.92 (2) |
| Si $-O_2$ | 1.65 | Ba $-O_1$ | 2.99 (2) | $O_1$ $-O_1$ | 2.67 (4) |
| $O_1$ $-O_1$ | 2.67 | Ba $-O_2$ | 3.11 (2) | $O_1$ $-O_1$ | 3.90 (8) |
| $O_1$ $-O_2$ | 2.61 (2) | Ba $-O_3$ | 2.91 (2) | $O_1$ $-O_3$ | 3.18 (8) |
| $O_2$ $-O_2$ | 2.62 | $O_1$ $-O_1$ | 3.20 (3) | | |
| $O_2$ $-O_2$ | 2.68 (2) | $O_1$ $-O_1$ | 3.22 (2) | | |
| Average | | $O_1$ $-O_1$ | 3.90 (2) | Average | |
| Si $-$O | 1.62 | $O_1$ $-O_2$ | 2.61 (4) | Ba $-$O | 3.03 |
| O $-$O | 2.65 | $O_1$ $-O_2$ | 3.45 (2) | O $-$O | 3.25 |
| | | $O_1$ $-O_3$ | 3.18 (4) | | |
| | | $O_1$ $-O_3$ | 3.55 (4) | | |
| | | $O_2$ $-O_3$ | 3.46 (2) | | |
| | | Average | | | |
| | | Ba $-$O | 2.88 | | |
| | | O $-$O | 3.17 | | |

The plan of the structure is shown in Fig. 2. The structural motif is most clearly revealed in the side projection (Fig. 3). The architectural basis of the structure of $Ba_5[Si_4O_{12}](OH)_2$ is determined by $Ba_1$ 10-vertex polyhedra (with 15 faces), which are linked by a twofold axis into pairs with a common rectangular face. Along the fourth-order axis the complexes, joining along triangular faces, combine into layers. Through vertices lying in the mirror plane, the layers are connected into a three-dimensional framework, which is compacted by

$Ba_2$ polyhedra. These are also 10-vertex polyhedra, but with 12 faces, and are arranged according to a body-centered law, with Ba at inversion centers. The Ba 12-hedra have 8 common triangular faces with the Ba 15-hedra.

According to the same body-centered law, but with a displacement along $c$ by 1/2, the highly symmetric ($4/mmm$) tetragonal silico-oxygen [$Si_4O_{12}$] rings are arranged; that is, the $Ba_2$ polyhedra and the centers of the four-membered rings occupy two different systems of inversion centers with multiplicity 2.

Both types of Ba polyhedra have common edges with Si–O tetrahedra. Genetically, the 10-vertex $Ba_1$ polyhedra are Thomson cubes with semioctahedra on the square faces. The $Ba_2$ polyhedra (12-hedra with 10 vertices), formed by a regular tetragonal prism in combination with a bipyramid, have long been described in the structure of $BaO_2$ ([6]). At the vertices of the semioctahedra in the $Ba_2$ polyhedra are OH groups. Each OH simultaneously participates in four $Ba_1$ polyhedra.

The [$Si_4O_{12}$] ring in $Ba_5[Si_4O_{12}](OH)_2$ possesses maximum symmetry, whereas the first four-membered baotite ring had only $\bar{4}$ ([7]). Four-membered rings have proved to be very characteristic structural units in Ba silicates. In addition to baotite, similar rings, but with monoclinic symmetry, have been found in taramellite $Ba_2Fe_2[Si_4O_{12}](OH)_2$ ([8]). In the structure of gillespite $BaFe[Si_4O_{10}]$, the [$Si_4O_{12}$] rings combine into wavy two-story layers ([9]). Isolated four-membered [$Si_4O_{12}$] rings have also been found in rare-earth kainosite ([10]).

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*Note: Figure translations are in progress. See original paper for figures.*